

**Assessment of the suitability of composted sewage sludge
as an adsorbent for the treatment of heavy-metal
contaminated wastewater, with special reference to
cadmium**

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ABSTRACT

A large proportion of sewage sludge in South Africa contains heavy metal concentrations which are deemed to be above threshold limits for its use as a fertiliser. Furthermore, sewage sludge has a high affinity for heavy metals. Until the sources of heavy metal contamination of municipal sewage sludge are considerably reduced the contaminated sewage sludge must either be disposed of or used for some other purpose. The use of contaminated sewage sludge as an adsorbent for treating heavy metal-contaminated wastewaters may provide an alternative and practical use for this material.

The objective of this study was to assess the potential of composted sewage sludge (which is more stable and has a higher permeability than ordinary sewage sludge), produced from municipal sewage sludge in Milnerton, as an adsorbent for the extraction of heavy metals from contaminated wastewaters. The study was conducted with specific reference to cadmium since it is one of the most toxic of the heavy metals and occurs in many types of wastewaters.

Preliminary investigations intended to characterise selected chemical and physical properties of composted sewage sludge were cation exchange capacity (CEC) determinations of four size fractions using the Gillman method, specific surface area measurements of four size fractions (BET method), particle size distribution (between size fractions > 2 , < 2 , $2-1$, $1-0.1$ and < 0.1 mm) and potentiometric titrations in the pH range of 3 to 10. It was found that properties such as surface area and CEC did not vary sufficiently with particle size to warrant a distinction (for further experiments) based on particle size beyond separating the > 2 mm fraction which consisted predominantly of wood chips. Potentiometric titration results revealed the presence of two predominant types of acidic functional groups in the composted sewage sludge which were assumed to be heterogenous mixtures of carboxylic acid and phenolic groups. Estimates of pK_a values for each of these groups and the total acidity of the bulk material were made (pK_a of carboxylic acid groups ≈ 6.5 ; pK_a of phenolic groups ≈ 8.3 ; and total acidity ≈ 300 mmol_c/kg). It was also noticed that the pH of aqueous suspensions of composted sewage sludge decreased with time, and the reason suspected for this behaviour may be that the organic matter is oxidised in the presence of air, resulting in the formation of acidic groups.

Cadmium adsorption experiments showed that composted sewage sludge can efficiently remove Cd from aqueous suspensions in which the Cd concentration range is 0 to 17 mg/L. Batch adsorption studies were used to determine the effect of pH, ionic strength and the nature of the background electrolyte on Cd adsorption. Cadmium adsorption was found to be at a maximum at pH values greater than 7.5 over a range of initial Cd concentrations of

2 to 10 mg/l. Almost no adsorption takes place below pH 3. Adsorption isotherm studies using three different background electrolytes (NaCl, Na₂SO₄ and CaCl₂) at varying concentrations yielded the following information : increasing ionic strength results in decreases in Cd adsorption; SO₄²⁻ has less of an inhibiting effect on Cd adsorption than does Cl⁻; and Ca²⁺ has a greater inhibiting effect on Cd adsorption than Na⁺.

The complexation capacity of composted sewage sludge with Cd, using the data obtained from the adsorption isotherm studies, was estimated for each of the batch experiments by the graphical solution of two different linear mathematical relationships. The highest complexation capacity estimate (at low ionic strength) was 10 g Cd/kg compost. Conditional stability constant (K_c) values for the formation of Cd-compost complexes (estimated by the graphical solution of a linear mathematical expression) showed that there are high concentrations of adsorption sites with low K_c values and low concentrations of adsorption sites with high K_c values, which was reflected in the observed higher efficiency of Cd removal from solution as Cd concentrations decreased (from 60 % at 16.5 mg Cd/l up to 95 % at 0.1 mg Cd/l). Complexation capacity and conditional stability constant values were consistent with the observed effects of background electrolyte cations and anions on Cd adsorption.

Desorption studies of Cd from the compost showed that the use of either HCl or H₂SO₄ has no significant effect on the desorption efficiency. Rather, the desorption efficiency is related to the initial adsorbed concentration of Cd and decreases with decreasing adsorbed Cd concentration. Desorption using HCl or H₂SO₄ results in a decrease in the complexation efficiency of composted sewage sludge with Cd by approximately 20 to 30 %.

A breakthrough curve obtained from a column experiment (internal diameter = 16 mm; length = 54 mm; containing 6 g of dry compost) using a Cd influent concentration of 5.5 mg/l (I = 0.05 M) at a flow rate of 80 ml/hr showed that breakthrough occurred when Cd loading of the compost was approximately 1.7 g/kg.

The results of this study suggest that scavenging of Cd (and probably other heavy metals too) from contaminated wastewaters is feasible using composted sewage sludge.

INTRODUCTION

Many countries in the world produce large amounts of sewage sludge. In South Africa this has been estimated at 800 tons per day dry mass (Water Institute of Southern Africa, 1993). There are several means of disposing of this sludge: ploughing into sacrificial land which then can no longer be used for agricultural purposes (47%); by stockpiling in dry heaps or in lagoons (20%); by dumping with municipal refuse (3.2%); by unspecified methods (2.3%); or in a beneficial manner, such as for fertilizer and brick-making (27.8%). The methods of disposal which are not beneficial have numerous environmental effects which are undesirable. For example, the ploughing of sewage sludge into agricultural land can lead to heavy metal contamination of crops and animal produce.

The non-beneficial disposal of sludge results primarily from the fact that a large proportion of the sewage sludge produced contains concentrations of heavy metals which are regarded as being too high. The sludge does not meet the criteria required for land application as a soil conditioner in terms of the current Department of National Health and Population Development (DNH & PD) guidelines (1991). A large proportion of the sludge fails due to cadmium concentrations exceeding the limit.

Less than 1% of the total flow of sewage to a treatment works is produced as sludge and this typically contains between 50 and 80% of the total quantity of Cd, Cu, and Pb entering the works (Lester *et al.*, 1983). These and other metals are concentrated in sewage sludge to a significant degree. The sludge therefore has a high affinity for the heavy metals as do many other biomass types. In fact, many biomass materials such as algae, yeast, natural peat, and even tree bark have undergone extensive trials in order to characterize them with respect to their biosorptive properties. Conventional methods of heavy metal removal from wastewater streams include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment and evaporative recovery. Such processes may be ineffectual or extremely expensive, especially when the heavy metals are in low concentrations. There is thus scope for the use of biosorbents which have a high affinity for, and a high efficiency of removal of, heavy metals at low concentrations.

In view of the fact that much of the sewage sludge produced in South Africa cannot be used as a fertiliser because of its heavy metal content and that it may have significant biosorptive properties, it would seem expedient to characterise it as a potential biosorbent for the

treatment of heavy metal-contaminated wastewater. In this way some potentially beneficial use may be found for sewage sludge which would otherwise have been disposed of in a non-beneficial manner. Of course the sludge would itself become more hazardous by loading it with heavy metals, and subsequent treatment, or safe disposal would be necessary.

The composting of sewage sludge in South Africa is a relatively new process which is currently being operated only at a single municipal sewage works which is in the Western Cape. The composting process is one in which humification of organic matter occurs. Humified organic matter contains a high concentration of humic and fulvic acids which contain functional groups that are efficient in complexing heavy metals. The composting process is also relatively cheap.

It was the aim of this study to characterize composted sewage sludge, which is currently being produced on a commercial scale at a local fertilizer company, as a potential biosorbent for the treatment of heavy metal contaminated wastewaters. The approach to this characterization was to quantify the extent to which this compost could remove heavy metals from solution, with specific reference to cadmium, and to study the effects that several experimental conditions might have on this interaction.

The scope of the study was restricted, due to limitations on time, with respect to the number of experiments which could be done in characterising the compost as a biosorbent. The tests which were performed on the compost were selected so as to give a general indication of its biosorptive properties. Only one heavy metal, namely cadmium, was used in the tests. The selection of cadmium as the metal of choice for the study was based on the fact that it is a highly toxic heavy metal which contaminates numerous types of wastewaters. For several reasons, as will be discussed further in this dissertation, the understanding of the interactions between the compost and a mixture of heavy metals would also be desirable, and further research in this area will eventually be necessary, so that the adsorption of heavy metals from real industrial wastewater effluents can be understood.

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1. CADMIUM GEOCHEMISTRY AND REMOVAL FROM WASTEWATER

1.1 General physical and chemical characteristics of Cd

Cd is a second row transition element in the zinc group and has an electronic structure of $[\text{Kr}]4d^{10}5s^2$. Its atomic mass is 112.41. The chemistry of Cd closely resembles that of Zn, and they usually occur together, although Cd usually is found in minor quantities relative to Zn. Some of the physical properties of Zn and Cd are listed below in Table 1.1.

Table 1.1 : Important physical properties of Cd and Zn.

Property	Zinc	Cadmium
Covalent radius (Å)	1.25	1.41
Ionic radius (Å)	0.74	0.95
Melting point (°C)	420	321
Boiling point (°C)	907	765
Density (g/cm ³)	7.14	8.65
Paulings electronegativity	1.6	1.7

When Cd is oxidised, the bivalent cation Cd^{2+} is formed. No other common oxidation states are found. Bonding in Cd(II) compounds exhibits a higher degree of covalency than most other transition metals. Cd forms oxides (CdO), sulphides (CdS), and halides (CdX_2) where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$, by heating Cd in the presence of O, S, or X respectively. The sulphides are sparingly soluble, amongst the halides the fluorides are much less soluble than the chlorides, bromides and iodides which are more covalent than the fluorides. The oxides of Zn and Cd differ in behaviour in that ZnO is amphoteric whereas CdO is largely basic. Addition of alkali to an aqueous solution of a Zn^{2+} salt first gives a precipitate of $\text{Zn}(\text{OH})_2$, which redissolves in excess alkali, forming zincates (eg. $\text{Zn}(\text{OH})_4^{2-}$). Only in very strong alkali does CdO show any acidic properties, forming for example $\text{Na}_2[\text{Cd}(\text{OH})_4]$. Of the

halides of Cd, only the chloride is of environmental importance. The halides are all soluble in water, and form complex ions such as CdX^+ , $\text{CdX}_2(\text{aq})$, CdX_3^- , and CdX_4^{2-} in solution in excess halide ion. The distribution of chloro-species in water (i.e. fraction of each species versus concentration of Cl^-) is given in Figure 1.1.

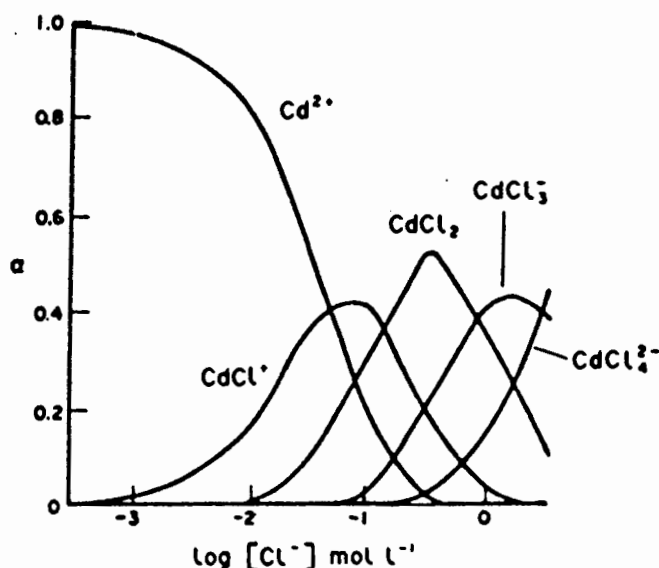


Figure 1.1 : Distribution diagram for Cd-chloro species (After Fergusson, 1991).

No complexes of Zn^{2+} and Cd^{2+} are known with pi-bonding ligands such as CO, NO, or alkenes. Zn and Cd do form complexes with CN^- , eg $[\text{Zn}(\text{CN})_4]^{2-}$. Zn(II) and Cd(II) occur largely as tetrahedral complexes, eg $[\text{M}(\text{NH}_3)_4]^{2+}$, $[\text{M}(\text{NH}_3)_2(\text{Cl})_2]$, $[\text{Zn}(\text{CN})_4]^{2-}$, and $[\text{Cd}(\text{pyridine})_2\text{Cl}_2]$, and also form several 6-coordinate octahedral complexes such as $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{M}(\text{NH}_3)_6]^{2+}$. The octahedral complexes of Zn are not very stable, but Cd forms octahedral complexes more readily and they are more stable than those of Zn because Cd is larger.

1.2 Uses of cadmium

In 1988 worldwide production was 22000 tonnes. This is much less than Zn production in the same year which amounted to 7.1 million tonnes. Cd is typically extracted from zinc rich ores, such as sphalerite, which contain traces of Cd.

Cd is principally used in protecting steel from corrosion. It is applied electrolytically by Cd plating. Cd absorbs neutrons very well and is used to make control rods for nuclear reactors. It is also used in nickel/cadmium storage batteries. CdS is an important, but expensive, yellow pigment which is used in paint.

1.3 Natural introduction of cadmium to the environment

1.3.1 Atmospheric

Natural processes, including aeolian transport of weathered rock particles, forest fires, volcanic emissions, transpiration, and also possibly volatilization of Cd from soils, all give rise to the injection of Cd into the atmosphere. Gases, vapours, and particles are deposited from the atmosphere by wet and dry processes. In general most particles and reactive gases and vapours are deposited within one month of injection and probably in less than half that time (Brewers *et al.*, 1987). The average natural flux of Cd through the atmosphere has been estimated to be 830,000 kg/year (Nriagu, 1979). The concentrations of Cd in aerosols and wet and dry atmospheric precipitation vary widely both in time and space, but it appears that Cd is considerably enriched relative to the major conservative constituents of source rocks, such as aluminium (Herron *et al.*, 1977).

1.3.2 Terrestrial and fresh-water

1.3.2.1 Distribution

Rivers and lakes are fed by water which has spent some time in intimate contact with the soil and subsoil. In the natural system it is expected that the Cd content of a soil is related to the parent rock from which it is derived (Vinogradov, 1959). Since soil is a ternary mixture, virgin weathering products such as soils should contain less Cd than the underlying bedrock. Similarly the Cd content of rivers and lakes should be related to the types of soil through which the drainage water has passed, though subject to later modifications due to physicochemical and biological processes (Brewers *et al.*, 1987). Analyses of Cd concentrations in several common rock types have shown that the ranges within a given rock type are wide, and there is considerable overlap between rock types. The widest range and highest concentration (0.3-0.11 mg/kg) are formed in sedimentary rocks, with igneous rocks

showing more uniformity in concentration at levels of 0.1-0.3 mg/kg (Brewers *et al.*, 1987). Continental crust has been estimated to contain about 0.1 mg/kg Cd (Heindrichs *et al.*, 1980). The mean soil Cd concentration has been estimated from 1642 soils from different parts of the world as 0.62 mg/kg, or 6 times greater than that estimated for the continental crust (Ure and Berrow, 1982).

1.3.2.2 Chemistry

Heavy metals are to a large degree immobilised by adsorption onto soils. Adsorption results usually fit either the Langmuir or Freundlich isotherms (Adriano, 1986; Asami, 1984). Factors that influence the adsorption are pH, ionic strength, competing cations and the constituents of the soil. The removal of organic matter from soil has been shown to reduce the adsorption capacity for Cd (Elliot *et al.*, 1986; Haas and Horowitz, 1986). The immobilisation of heavy metals by organic matter in soils can be offset to some degree by their mobilisation through the formation of complexes with soluble organic matter, and this phenomenon is particularly pronounced at low total metal concentrations in the soil (Neal and Sposito, 1986).

The chemistry of Cd in fresh water is highly complex depending on its speciation, which in turn is dominated by the oxidation status and the pH of the medium, as well as on the concentrations of numerous organic and inorganic anions and other metal cations. It is generally accepted that many of the more important trace metals form complexes with organic or inorganic ions or molecules under conditions typical of natural waters (Stumm and Morgan, 1970; Manahan, 1972). Formation of complexes involves the substitution of one or more of the water molecules from the inner hydration sphere of the metal ion by the complexing agent or ligand. The properties of complexed ions may be very different to those of uncomplexed ions. In most cases, further chemical reaction, resulting in precipitation as an insoluble salt or adsorption on solids, can occur only via the hydrated metal ion, and complex formation has the effect of suppressing such a reaction by reducing the concentration of "free" metal ion (Gardiner, 1975). It cannot be assumed, however, that the complex is unreactive. A complexed ion can be adsorbed more strongly on a surface than the hydrated ion (Stumm and Bilinsky, 1973).

Cd^{2+} in natural waters is complexed to various degrees with different ligands found in these systems. Ligands which predominantly complex with Cd^{2+} in natural waters are OH^- , CO_3^{2-} , Cl^- , SO_4^{2-} , and humic compounds. Complexation with other ligands is usually negligible except, for

example, when unusually high concentrations of CN^- or PO_4^{3-} could result in increased complexation. The degree of complexation of Cd^{2+} with each of these ligands is determined by the concentration of these ligands in the water. The concentration of ligands in water depends on the origin of the water. This relationship was shown by Gardiner (1975), who took water samples of different origins, spiked them with varying concentrations of Cd, and compared the speciation of Cd in each of the samples. This relationship is shown in Figure 1.2. The results showed that in ground-water from a chalk aquifer, Cd is predominantly uncomplexed. In addition, the ground-water contains very little organic matter which could complex the Cd. The increase in the extent of complexation in the other samples is mainly due to the higher concentration of humic material, but is also partly due to the higher pH value and to increases in chloride and sulphate concentrations. Gardiner also found that the extent of complex formation is independent of total Cd concentration in the concentration range of 0.1 to 1.0 mg/l. Gardiner speculates that the extent of complex formation would be greater at lower Cd concentrations because strong are present complexing ligands present at very low concentrations and would become saturated at higher trace metal concentrations. Interestingly, the extent of complexation may increase at lower Cd concentrations since each compound constituting the mixture could form a complex with a different stability constant, and the more active compounds would preferentially form complexes at low metal concentrations.

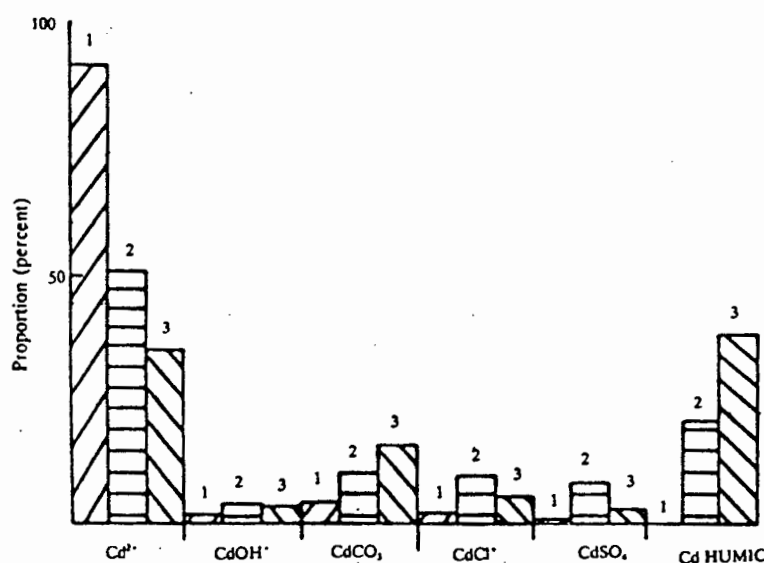


Fig. 1.2 : The complexation of cadmium in three filtered natural water samples. Added cadmium concentration 0.1 to 1.0 mg/l. 1) Fresh ground water from a chalk aquifer. 2) Water from R. Lee, downstream of a sewage treatment works. 3) Secondary domestic sewage effluent.

The mobility of Cd in soil pore water and ground water is strongly controlled by precipitation (as CdCO_3 and CDs) and by adsorption by soil particles, clay minerals, organic matter, and the hydroxides of iron and manganese (Brewers *et al.*, 1987). Adsorbability is generally greatest for iron hydroxides and least for clay minerals. The presence of complexes of Cd, however, can considerably reduce adsorption by all of the above materials, and the presence of other cations can further reduce Cd adsorption (Brewers *et al.*, 1987). Furthermore, macro and micro fauna can significantly affect the mobility of Cd in soil and ground water.

1.4 Anthropogenic inputs of Cd to the environment

Cd contamination of the environment has been attributed to several sources, which are classified as being either primary or secondary sources. Primary sources include fertilisers and sewage sludge. Secondary sources include smelters, refuse incinerators, mining areas, fossil fuel combustion, tyre wear, weathering of paint, rubbish disposal and long range aerosol.

1.5 Chloride, hydroxide, and carbonate speciation.

The inorganic speciation of Cd in water is similar to that of lead, but is simpler because the free cation can exist up to relatively high pH values i.e. pH 7-8 (Eichenberger and Chen, 1982; Gardiner 1974). For this reason it is a major component of fresh waters and a significant component of sea water. The hydroxy species only persists down to a pH of 8-9 (Figure 1.3) below which the Cd^{2+} cation occurs (Hahne and Kroontje, 1973). From the data in Figure 1.1 it appears that Cd-chloro species are the major components in seawater ($[\text{Cl}^-] \approx 0.54 \text{ mol/l}$), especially CdCl_2 , CdCl_2^- , and CdCl^+ , at pH values of 7-9 (Hahne and Kroontje, 1973; Florence, 1986; Kester, 1986). In more dilute systems however ($[\text{Cl}^-] \approx 0.01\text{-}0.03 \text{ mol/l}$) the Cd^{2+} ion begins to dominate. The Cd-chloro system is relatively stable, one reason for which is the strong Cd-Cl bond (Moore and Ramamoorthy, 1984).

The CdCO_3 ion-pair in solution is not as significant as for the corresponding lead species. Calculated amounts, in a variety of freshwaters, range from 4-21% (Raspor, 1980). The amount of CdCO_3 will depend on the pH of the water (Raspor, 1980) and the alkalinity. The higher the alkalinity, the greater the amount of CdCO_3 expected (Dyrssen and

Wedborg, 1980). Cd-carbonate formation has been shown to be negligible at pH = 6, but becomes more significant at pH values > 8 (Stumm and Brauner, 1975).

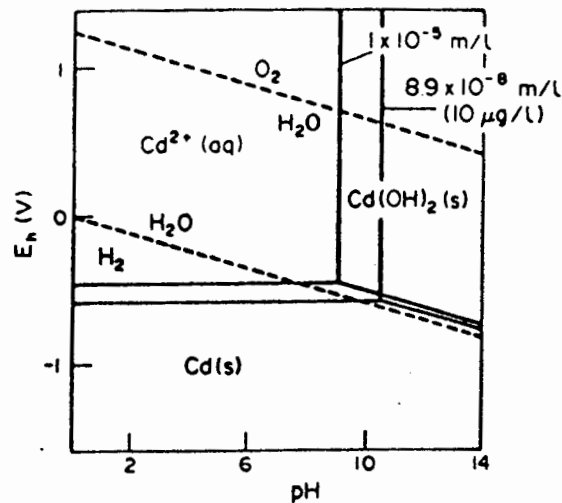


Figure 1.3 : E_h -pH diagram for Cd/H₂O system.

1.6 Human exposure to Cd

1.6.1 Exposure routes

Humans are exposed to Cd through food, which, depending on its origin can contain varying concentrations of Cd. Plants grown on soils containing significant concentrations of Cd tend to accumulate Cd. The Cd in these plants is then accumulated by animals eating those plants. Human consumption of plant matter with high concentrations of Cd, or of animals which have been eating plants with high Cd concentrations may lead to the accumulation of Cd in the human body which can ultimately have serious health effects such as those described in Section 1.6.2. Another exposure route is through household water which can leach Cd from the distribution systems (Fergusson, 1991). It is for these reasons that restrictions have been placed on the permissible concentrations of Cd in phosphate fertilisers (only in some countries), in sewage sludge applied to agricultural land as a soil ameliorant, and in industrial wastewater effluent.

1.6.2 Health effects of Cd ingestion

Cd has a relatively long lifetime in the human body (20-30 years), and thus tends to accumulate with time. It enters the human body through ingestion. It has different residence times in the body depending on location, for example the half life of Cd in the blood is considerably shorter than in the kidneys.

The percentage absorption of Cd from the diet is typically less than 5% (Bowen, 1975) but under certain nutritional conditions such as low Ca intake, values as high as 10% may be reached (Friberg *et al.*, 1974 ; World Health Organisation, 1975).

Cd is a suspected carcinogen, and under certain conditions can give rise to a severe bone disease (osteomalacia, also known as Itai-itai disease), which is secondary to kidney damage.

Zn has an important biological role in the enzyme systems of animals and plants. There are approximately 20 enzymes which contain Zn. Since Cd has a similar size to, and because it possesses the same electron distribution in the outer orbitals as does Zn, it is easily substituted for Zn in many enzymes thus preventing them from properly functioning.

1.7 Humic matter-cadmium interactions

1.7.1 Characterisation of humic materials

Humus can be subdivided into a) amorphous brown-coloured polymers, and b) compounds which are recognisable as either polysaccharides, polypeptides and lignins (McBride, 1994). The amorphous polymers are termed humic substances, which consist of irregular two or three dimensional arrays of condensed and broken aromatic rings with no identifiable monomer units (Gamble *et al.*, 1970) (Wright and Schnitzer (1961) and deBorger (1969) found that 48-67% of carbon atoms in fulvic acids are aromatic). Humic substances are further subdivided into three groups, namely humic acid, fulvic acid, and humin (McBride, 1994) according to their solubility in strong acid and base. Aqueous NaOH extracts humic and fulvic acid from soils, leaving humin unextracted. Acidification of the extract causes the humic acid to precipitate, while the fulvic acid remains soluble. This method does separate the polymeric materials

in terms of their more important chemical properties. It has been noted that fulvic acids from different sources show a surprising degree of uniformity in their properties (Burgess *et al.*, 1964). Table 1.2 summarises some of these properties. The fulvic acid-humic acid-humin sequence represents a continuum of properties with increasing resemblance to lignin which is a complex aromatic polymer (McBride, 1994).

Table 1.2 : Properties of humic substances.

	Fulvic acid	Humic acid	Humin
Molecular wt.	1000-5000	10000-100000	> 100000
%C	42-47	51-62	> 62
%O	45-50	31-36	<30
%N	2.0-4.1	3.6-5.5	>5
Acid content (moles/kg)	14	5	<5

(Table from McBride, 1994)

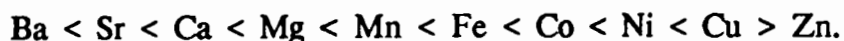
It should be noted that the size of the molecules, or aggregates, is influenced by pH, ionic strength, and the concentration of fulvic acid (Linder and Murray, 1987).

The chemical properties of humic and fulvic acids can largely be attributed to the presence of functional groups on these acids. A wide variety of functional groups exist on these acids and one of the reasons for their heterogeneity, besides the range in sizes, is that the distribution of the functional groups is varied.

1.7.2 Bonding types involved in cation adsorption

Organic matter-metal complexes involve two distinct types of bonding. In the first type of bonding, the complexes contain inner sphere bonds which have a certain degree of covalency. Evidence for the formation of inner-sphere complexes is implied by experimental results which show that a high degree of selectivity for certain metals is exhibited by organic matter (McBride, 1994). Also, this type of bonding results in a tendency towards

irreversibility or a desorption rate which is orders of magnitude slower than the adsorption rate. The strength of the bond is related to the chemical properties of the metal as well as the organic coordinating group (McBride, 1994). For any particular type of Lewis base, metals of smaller radius generally form the stronger complex. Thus metals of smaller radius form stronger bonds with O, N, and S in organic matter than do metals of larger radius. This concept gives rise to the Irving-Williams series of complexing strength for divalent metal ions :



An affinity sequence of soil organic matter for metals can also be described in terms of electronegativity, with metals of higher electronegativity being adsorbed more strongly. An observed order of affinity for divalent metal ions for soil organic matter related to electronegativity (in parentheses) is as follows : Cu (2) > Ni (1.91) > Pb (1.87) > Co (1.88) > Ca (1.00) > Zn (1.65) > Mn (1.55) > Mg (1.31). The affinity of humus for the essential macronutrients Ca^{2+} and K^+ is higher than electronegativity would predict, suggesting that certain complexing or chelating groups in humus select these metals on the basis of ionic size, which is what the Irving-Williams series predicts. The metals listed first tend to form inner sphere complexes with organic matter while those toward the end of the list are inclined to retain a hydration shell and remain freely exchangeable (Stumm, 1981; McBride, 1994).

Selectivity sequences for the adsorption of heavy metals by a wide range of cation exchange materials have been characterised, such as goethite : Mn < Co < Zn < Cu (Grimme, 1968) and Cd < Co < Zn < Pb < Cu (Forbes *et al.*, 1976); silica : Cd < Cu < Pb < Fe(III) (Schindler *et al.*, 1976); and by Fe-hydroxide gel : Co \leq Cd < Ni < Zn < Cu < Pb and by Al-hydroxide gel : Cd \leq Co < Ni < Zn < Pb < Cu (Kinniburgh *et al.*, 1976). Furthermore Abd-Elfattah and Wada (1981) found a selectivity sequence of Cd, Co < Zn < Cu \leq Pb for the adsorption onto soils. These sequences are correlated neither with ionic radii nor with electron negativity. The reason why the observed selectivity series is not as would be expected is largely because selectivity depends on a number of factors beyond the properties of the metals themselves. Metal-humic interactions would not be expected to strictly adhere to the above-mentioned selectivity rules since several other factors play important roles in the selectivity, including :

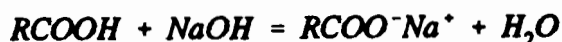
- a) the chemical nature of the organic ligands (type of functional group),

- b) the level of adsorption on the organic matter,
- c) the pH at which adsorption is measured (some metals compete more effectively with H^+ for bonding on functional groups than do others),
- d) the ionic strength of the solution in which adsorption is measured (this determines the intensity of competition by other cations for the complexing sites).

The second type of bonding involves the formation of freely exchangeable organic matter-metal complexes. In this type of bonding, the negatively charged surface of organic matter can also function as a weak-field exchanger (ie. adsorption can occur by non-selective electrostatic forces). The charge and radius of metal ions are the factors which control the selectivity of the adsorption, with larger cations tending to preferentially displace small cations (McBride, 1994). The reason for this is that smaller cations tend to be more strongly hydrated than larger cations resulting in an effectively larger radius which limits the distance of closest approach.

1.7.3 Humic substance response to pH

The predominant functional groups of soil organic matter contain oxygen atoms, with the carboxylic and phenolic groups accounting for most of the titratable acidity in humus. These organic groups dissociate by reaction with base :



This reaction results in the generation of negative charge on the surface which is balanced by the cations which are consequently adsorbed on the surface. Carboxylic acids are more acidic than phenols and are thus responsible for a large proportion of the CEC attributed to organic matter in soils (McBride, 1994). It is evident that the charge generated on the surface of humic substances is pH dependent. A simple monoprotic dissociation model has been used to describe the pH dependent charge on humus where the organic acid HA forms the anion A^- :



The acid dissociation constant, K_a , is defined by :

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

and if α is the degree of dissociation of the acidic functional group then :

$$\alpha = \frac{[A^-]}{[HA] + [A^-]}$$

and the expression:

$$pH = pK_a + \log \frac{\alpha}{1 - \alpha}$$

can be derived.

This equation correctly describes the titration curve of soluble monoprotic acids which can be represented by Figure 1.4 .

Soil organic acids are however often in the solid or colloidal form, and not dissolved in water. They are also heterogenous, with various acidic functional groups possessing different pKa values. They are also polymeric and polyprotic. It is for these reasons that the equation based on a simple, dissolved, monoprotic acid does not correctly describe the dissociation behaviour of humic substances. The polymeric and polyprotic properties of the humic substances complicate the model because of the fact that successive removal of protons from a single molecule becomes increasingly less likely (McBride, 1994). This explains, in part, the lower dissociation compared to a single monoprotic acid at high pH (Figure 1.4). Figure 1.4 illustrates that humic acid dissociates in a more linear fashion in response to pH increases than does the single monoprotic acid.

Since dissociation creates exchange sites, α is related to the cation exchange capacity (CEC) of organic matter by the simple equation :

$$\alpha = \frac{CEC (actual)}{CEC (potential)}$$

where CEC (potential) is the sum total of the acidic functional groups in the soil organic matter. Accordingly, an α -pH relationship such as that described in Figure 1.4 can be used to estimate the CEC of organic matter at any pH. For example, at pH 7, the CEC is given by

$$CEC (pH\ 7) = \alpha (pH\ 7) \times [total\ organic\ acid\ content]$$

The organic acid content of the organic matter can be measured by titration with base.

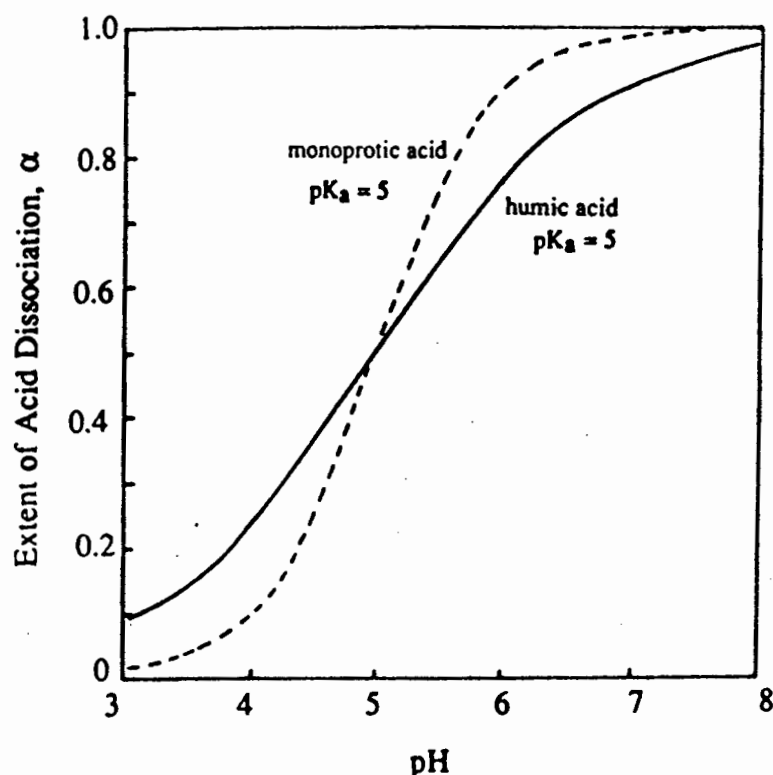


Figure 1.4 : The effect of pH on dissociation, α , of a humic acid and simple monoprotic organic acid in solution, both with pK_a of 5, calculated from the Henderson-Hasselbach equation (McBride, 1994).

1.7.4 Ionic strength effects on adsorption

Compounds which are ionic in the solid state should, of necessity, be completely ionic when dissolved. However, because of forces of electrostatic attraction, each cation in solution will, in effect, surround itself with an 'atmosphere' of anions, and each anion will surround itself with an 'atmosphere' of cations. These forces of interionic attraction then prevent each ion from moving independently and, thereby, render it less effective in altering the properties of the solvent or solution. The effective concentration of the ions in solution is thus best expressed by their activities rather than by their concentrations. The activity of any ion, a_i , is related to the concentration, c_i , by the activity coefficient, γ_i .

$$a_i = \gamma_i c_i$$

The Debye-Huckel theory of activities recognizes that ions of opposite charge tend to surround and electrostatically stabilize any particular ion in solution. The theory stems from the observation that the mean activity coefficient, γ_{\pm} , of a strong electrolyte is the same in all dilute solutions of the same ionic strength regardless of ionic composition. The ionic strength can be defined by the equation

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

where c_i = concentration of the i th ion in solution and z_i = charge of the i th ion in solution. Ionic strength, I , is a measure of the nonideality that the solution imposes on any dissociated electrolyte. Solutions with higher ionic strength are less 'ideal' in the sense that individual ions interact more strongly with neighbouring ions of opposite charge. This electrostatic attraction generally lowers the effective concentration of ions. The extended Debye-Huckel equation, which applies for ionic strengths of less than 0.1, is given by

$$\log \gamma_{\pm} = -0.5091 Z_{\pm}^2 \sqrt{I}$$

The efficiency of adsorption of metals onto humified substances increases with decreasing initial metal concentrations (Viraraghavan and Dronamraju, 1993). Furthermore, the amount of adsorption of a solute onto an adsorbing surface is concentration dependent. The ionic strength thus plays an important role in determining the effective ion concentrations in solution and hence in the adsorption.

The nature of the ionic species in solution is also of importance in determining the chemical behaviour of Cd since ion pairing between Cd and anionic species occurs in solution, affecting the behaviour of Cd. For example, chloride ions in solution have much greater effects in decreasing Cd adsorption onto humic substances than do sulphate ions. Similarly, the nature of the cations in the solution affect adsorption since they have different abilities to compete with Cd for adsorption sites. For example, calcium competes much more strongly than does sodium for adsorption sites on humic substances.

1.8 Treatment of heavy metal contaminated water

1.8.1 Conventional methods

Large amounts of heavy metals are released into the environment from industrial waste-waters. The heavy metals enter the waste-water streams through technological activities used directly in the processing of metals or through other routes. Industrially based metal-bearing discharges can be considered as point source emissions which offer the possibility of feasible remedial actions (Volesky, 1994).

Conventional methods of metals removal from aqueous solutions before they are disposed of include :

- a) chemical precipitation and sludge separation,
- b) chemical oxidation or reduction,
- c) ion exchange,
- d) reverse osmosis,
- e) electrochemical treatment,
- f) evaporation,

1.8.2 Biosorption

Biosorption is the adsorption and/or complexation of dissolved metals based on the chemical activity of biomass (Volesky, 1994). This type of metals removal system is becoming increasingly attractive as regulations on heavy metal concentrations in waste-water are becoming more and more stringent, resulting in the cheap technologies becoming inadequate (Braukman, 1990) while more effective methods are more costly. Biosorption thus seems to be an attractive solution since cheap and easily accessible biomass, with a high adsorptive capacity for many heavy metals is a very cost effective means of cleaning contaminated waters.

Types of biosorbents that have been used include yeast cells which are byproducts of large scale industrial fermentations, certain metal binding algae found in large quantities in the sea, mycelia of fungi, various forms of coal, peat, and tree bark. Lead and cadmium are efficiently bound from very dilute solutions by the dried biomass of marine algae such as

Ascomyces and *Sargassum* which can accumulate 30% of biomass dry weight in the metal (Volesky, 1994). Also, mycelia of industrially steroid-transforming fungi *Rhizopus* and *Absidia* have been found to be excellent biosorbents for Pb, Cd, Cu, Zn, and U, binding also other heavy metals up to 25% of the biomass dry weight (Volesky, 1994).

1.8.2.1 Sewage sludge as a biosorbent

Studies have been conducted from which it has been shown that the activated sludge treatment process is capable of reducing metal ion concentrations in waste water (Sterritt *et al.*, 1981), and other studies have shown that waste activated sludges from a variety of sources are capable of biosorbing several metal ion species from solution (Kasan, 1993; Swalaha and Kasan, 1992).

The reduction in metal ion concentrations in the activated sludge treatment process has been attributed to physico-chemical interactions between metal ions and sludge surfaces (Bux and Kasan, 1994; Sterritt *et al.*, 1981; Stoveland and Lester, 1980). Sludge surfaces are polymeric in nature, comprising of protein, carbohydrate, nucleic acids and lipid (Goodwin and Foster, 1985). Sludge biomass is negatively charged due to the ionisation of acidic groups such as carboxylic, hydroxyl, sulphate and amino groups (Hughes and Poole, 1989). The nature and concentration of ionogenic materials present at sludge surfaces have been shown to determine the magnitude of the sludge surface charge (Horan and Eccles, 1986). Studies are currently examining the relationship between the surface negative charge on the sludge and its capacity to biosorb a variety of metal ions from solution.

In a study of metal binding characteristics of raw, activated, and anaerobically digested sewage sludges, (Lake *et al.*, 1989) it was found that the stability of complexes formed in each sludge type followed the general order $Cu > Pb > Cd$. Cd exhibited similar stability constants in each sludge type, while more stable complexes of Cu and Pb were found in the treated than in the raw sludges. It was also found that the capacities of raw and digested sludges to complex all three metals decreased as particle size increased. However the converse was true for activated sludge, particularly for Cu. This suggests a lesser contribution from surface area phenomenon in metal complexation by activated sludges (Lake *et al.*, 1989). Two types of complex was formed by each metal, the first having higher stability constants than the second. This indicates that at low metal ion concentrations the complexation was controlled mainly by stronger bonding sites whereas at high metal ion concentrations the stronger sites become fully occupied and weaker sites

started to affect complexation. This phenomenon can probably be ascribed to the inner and outer sphere bonding modes described in Section 1.7.2. Also found by this study was that the concentrations of binding sites available for participation in the second type of complex were greater than those available for participation in the first type.

1.8.2.2 Humified organic matter as a biosorbent

Studies using brown coal, oxyhumolite (a postsedimentary oxidised subbituminous coal containing humic substances capable of interacting with metal ions), and peat have previously been conducted to determine their ability to remove heavy metals from waste waters (Horacek *et al.*, 1994). It was also shown in this study that the calcium loaded forms of these materials could be effectively used for metal extraction (Pb, Cu, and Zn) by ion exchange with calcium and Horacek *et al.* (1994) recommended this material for the removal of metals from solutions with concentrations of less than 0.01 mol/l. The selectivity for all the adsorbents used were found to be in the order of $Pb > Cu > Zn$, and the cation exchange capacities for the materials varied in the following order oxyhumolite (73) > coal (65) > peat (63) {values in parentheses denote the CEC in mg Ca/g adsorbent}. Additionally it was found that for Cu^{2+} the adsorption efficiency increased with decreasing metal concentrations. The same phenomenon was observed by Viraraghavan and Dronamraju (1993) who conducted a similar study in which they determined the effectiveness of peat in adsorbing Cu, Ni, and Zn from wastewater, and the effects of contact time, pH, initial concentration of the adsorbate, and temperature on adsorption. This was explained by Horacek *et al.* (1994) as resulting from the partial hydrolysis of the cupric salt at higher concentrations.

Viraraghavan and Dronamraju (1993) found that a contact time of two hours was necessary for the adsorption to reach equilibrium, the optimum pH was found to be between 4.5 and 5.0. They also found that the adsorption of Cu, Ni, and Zn was described well by both the Langmuir and Freundlich isotherms, and that the peat was effective in removing the heavy metals which they studied from wastewater solutions.

1.9 Conclusions

Cadmium occurs widely in the environment and is introduced in a dilute form over large areas by natural means and in a concentrated form over localised areas by anthropogenic input. Speciation is an important factor which determines the mobility and availability of Cd. The most common and dominating species of Cd in the environment are Cd-chloro and Cd-organic matter species.

Organic matter has a high affinity and capacity for Cd adsorption. This has been shown by biosorption studies as well as by studies of Cd mobility in the environment. Two types of sites for Cd bonding are available on organic matter : strong inner-sphere bonds which have a high degree of covalency and weaker outer-sphere bonds which are predominantly electrostatic in nature. Cadmium is typically less strongly adsorbed onto adsorbing materials than many other common heavy metals such as Cu, Ni, Zn, Pb and Fe.

Adsorption of Cd onto humic materials increases with increasing pH and increasing initial metal concentration. However, the efficiency of removal increases with decreasing initial metal concentrations. Competition between inorganic ligands in solution and the bonding sites on organic materials for heavy metal complexation results in a decrease in metal adsorption on the organic material as the concentration of inorganic ligands increases.

Biosorption is a cheap and attractive means of treating heavy metal-contaminated wastewaters provided that a cheap and easily accessible biomass, with a high biosorptive capacity for heavy metals, is available. Sewage sludge has been shown to be capable of adsorbing several metal ion species from solution. In addition, there is an excess of sewage sludge in South Africa (Section 2.1) which cannot be used as a fertiliser for reasons discussed in Section 2.4. Thus the use of sewage sludge as a biosorbent for the treatment of heavy metal-contaminated wastewaters may be an attractive alternative use for some of the excess sewage sludge produced.

2. SEWAGE SLUDGE IN SOUTH AFRICA

2.1 Quantities produced

The amount of sewage which passes through sewage treatment plants daily in South Africa has been estimated as 800 t/day dry mass (Palmer *et al.*, 1993; Water Institute of Southern Africa, 1993). Local and regional authorities, particularly in the rapidly growing larger town and metropolitan areas with increasing demand for provision of services are needing to find new ways whereby sludge produced at sewage treatment plants can be disposed of. The methods used for disposal are discussed in Section 2.4.

2.2 Characterisation

Sludge produced at wastewater treatment plants is a putrefactive, concentrated aqueous suspension of particulate organic material containing mainly biodegradable, but also inert substances. Its organic putrefactive nature makes it potentially both a public nuisance and a health hazard. It is very active biologically and if allowed to biodegrade in an uncontrolled way, it rapidly generates unpleasant odours and provides a site for insect and vermin breeding which can spread diseases by being carriers of pathogens present in the sludge. Being of human origin, the sludge contains many pathogens to man. Also, depending on the industrial contribution to the municipal wastewater, the sludge contains trace metals and elements such as Cd, Co, Cr (III), Cu, Hg, Mo, Ni, Pb, Zn, Se, B, As and fluoride. The sludge can also contain toxic organic compounds such as pesticides, polychlorinated biphenols (PCB's), polycyclic aromatic hydrocarbons (PAH's), dioxins, and phenolic compounds.

2.3 Treatment

Raw sludge has large amounts of organically bound energy, and for this reason cannot be applied to land because its biological activity would result in a high oxygen demand. The high oxygen demand creates anaerobic conditions in the soil and destroys the aerobic root

zone which plants require for growth. For this reason sludge is stabilised before being disposed of. This stabilisation can be done either aerobically or anaerobically. Generally during stabilisation, about 40% of the organic material in the sludge is oxidised and its oxygen demand reduces to around $1\text{g O}_2 / \text{kg total solids} / \text{h}$. After stabilisation the sludge is dewatered to concentrate the remaining organic and inorganic material further to reduce its volume and to make it easier to handle for disposal.

2.4 Disposal

Most sewage sludge is disposed of by land application, land filling, lagooning, co-disposal with solid wastes (garbage), ocean disposal, or incineration.

Land application, which is the controlled spreading of sewage sludge into or onto the surface of soils, has over the years become by far the most popular means of sludge disposal because of its nutrient value to the soil and its economy as a disposal option. Soils experiments have demonstrated that sewage sludge serves as a low grade fertiliser, typically with a 4-2-1 % N, P, K (nitrogen, phosphorus, potassium) ratio. It improves soil fertility, adds trace metals and elements as well as the N, P, and K, improves soil moisture-holding capacity and provides soil structure (Easton, 1983; Korentajer, 1991).

There are several environmental and health implications of land application of sewage sludge, these being 1) ground water pollution, 2) aerosol production (odours) and 3) food chain contamination. The first two issues can be easily dealt with by applying the sludge in a liquid form, below the soil surface during ploughing. This stops the production of odours. There is little chance of ground water contamination since at the maximum application rate of 8 t/ha/yr , at 5 % solids, is equivalent to 20mm of rain, which if applied at the right time of year, the soil can absorb very easily. Most of the organic and inorganic constituents are either of low solubility or are insoluble so that rainfall does not leach out the constituents to pose a ground water pollution threat.

Food chain contamination is of major concern. There are two main exposure routes through which man can be endangered by the trace metals and elements in the sewage sludge. These are either through the ingestion of contaminated crops or the consumption of organ

meats (liver, kidney) of animals which have grazed crop lands treated with sewage sludge. There are three categories of trace elements and metals with respect to environmental and health considerations :

- 1) Ones so sparingly soluble or strongly adsorbed by the soil or immobile in plants that plant shoots show very little increase even when the soil is enriched in these i.e. Ag, Au, Cr (III), Ga, Hg, F, Pb, Pt, Si, Sn, Zr.
- 2) Ones which cause phytotoxicity at concentrations in edible plant tissue below levels injurious to human or animal consumers i.e. Al, As, B, Ba, Be, Cu, Mn, Ni, and Zn.
- 3) Ones which accumulate to levels in plants harmful to humans or animals without visibly affecting the crop growth or yield i.e Cd, Mo, Se, Co.

Note that these categories overlap to some extent, and some of the trace elements listed could belong to more than one category, depending on various factors such as soil conditions and plant type.

Cadmium is the most important element in category 3 since it is present in many wastewaters which originate from industrial processes, and also because it is toxic at relatively low concentrations. The Department of National Health and Population Development (DNH & PD) guidelines (1991) specify the maximum permissible concentrations of a range of metals in sewage sludge to be used as a soil conditioner. These guidelines were developed in considering the properties of the metals in their toxicity, their uptake by plants, and also to which of the above three categories (listed above) the metals belong to.

Sewage sludge can be classified into four groups, types A, B, C, and D, depending on whether it has been stabilised, pasteurised, and with respect to metal content. Type D sludge has been stabilised, pasteurised, and has metal concentrations below specified values, so that at a maximum land application rate of 8 t dry mass / (ha.year) soil metal limits are not exceeded (DNH & PD, 1991).

Smith and Vasiloudis (1989) characterised the inorganic chemical content of South African municipal sludges. Twelve major inorganic contaminants were identified as commonly present in sewage sludge and their levels were determined in air dried sludge from 77 South African sewage works which had a total production of sewage sludge of 475 t/d dry mass. More than 60 % of the 475 t/d dry mass of sewage exceeded the specified limits of the 1991 guidelines (DNH & PD) in at least one metal.

2.5 Composting of sewage sludge

Composting of sewage sludge at the Milnerton Sewage Works is effected in the following way (Mike Bremmer, Kynoch Fertilisers : verbal communication) : raw sewage sludge is dewatered to approximately 45 % moisture content and then mixed with wood chips such that the sludge : wood-chip ratio is approximately 1 : 3. Wood-chip addition increases the C : N (carbon : nitrogen) ratio to approximately 30 : 1 enabling enhanced microbial activity for the composting process. Aerobic microbial action which occurs during composting generally decreases the C : N ratio to approximately 15 to 20 : 1.

The raw sewage sludge-wood chip mixture is then placed in aerated piles (aeration is by means of a pipe which is under the pile and which draws air through the pile). The piles are covered with previously composted sewage sludge to prevent unpleasant odours from escaping, and the breeding of vermin. Aeration enhances rates of microbial breakdown of the sludge-wood chip mixture. Microbial breakdown is an exothermic process causing the internal temperature of the piles to increase up to 55 to 65 °C during composting. This temperature is maintained for a period of 5 days, followed by a short maturation process to ensure that the reaction process is substantially complete. The high temperature which the sludge reaches during composting results in the effective pasteurisation of the sludge rendering it pathogenically harmless.

The resulting compost is then filtered through a mesh to remove the larger wood chips which are reused in subsequent composting of raw sewage sludge. The resulting compost is then marketed.

2.6 Conclusions

Sewage sludge disposal is a growing problem due to the rapid growth of urban areas. A large proportion of this sewage sludge contains heavy metals which are present in concentrations which are higher than the threshold limits for its use as a fertiliser. Alternative uses for this sewage sludge, such as brick making, have been found although only a very small proportion of sewage sludge is disposed of by these means. The common, non-beneficial methods of disposal of sewage sludge are becoming less environmentally

acceptable and the finding of alternative uses for sewage sludge are becoming more attractive. The use of sewage sludge as a biosorbent for the treatment of heavy metal-contaminated wastewaters may be an attractive alternative use.

Composted sewage sludge is a pathogenically inert and highly permeable material relative to raw or digested sewage sludge. Composted sewage sludge may therefore be a more suitable material for use as a biosorbent compared to ordinary sewage sludge.

3. CHEMICAL AND PHYSICAL CHARACTERIZATION OF COMPOST

3.1 Introduction

In order to understand as fully as possible the manner and extent of cadmium adsorption by composted sewage sludge, an appropriate characterization of the compost itself is necessary. In this chapter, a preliminary investigation of selected physical and chemical properties of the compost is reported upon.

3.2 Material

Composted sewage sludge, which was prepared according to the method described in Section 2.5, was obtained from Kynoch Fertilizer Ltd. in August 1995. The compost obtained was moist, and contained a large amount of partly decomposed wood chips.

Compost produced at the Milnerton Sewage Works by Kynoch Fertilizer Ltd., has on three occasions been analyzed by the CSIR for a wide range of constituents. These are reported in Table 3.1. The results however, do not necessarily reflect the composition of the compost which was obtained for this research, since the analyses were of samples obtained from different batches. The analyses were performed on the bulk compost, and not solely the < 2 mm size fraction, which was used exclusively in the adsorption work described in Chapter 4. Table 3.1 does however, give an approximate reflection of the chemical composition of the compost, and indicates that there is considerable variation between samples taken at different times. This is particularly true for the heavy metal concentrations.

High concentrations of Fe, Zn, and Mn were found, as opposed to very low concentrations of Cd. No tests were done, however, in this project to determine the form in which these metals exist in the compost (i.e. the proportion which is adsorbed by the compost).

Table 3.1 : Bulk chemical analyses of composted sewage sludge.

analyte	Date		
	23 July 1993	6 January 1994	4 July 1994
Total solids %		66.2	25.5
Volatile solids %		55.5	77.6
Moisture %		33.8	74.5
Carbon %	35.4	30.8	43.1
TKN* as N (g/kg)	8.8	13.5	17.9
Tot. P (g/kg)	1.7	3.1	2.3
K (g/kg)	1.3	1.2	7.5
Ca (g/kg)	22.2	28.2	
Mg**	1.3	1.5	
Cd	1	<1	
Co	3	4	
Cr	34	68	
Cu	61	109	
Fe	4906	11761	
Hg	<1	<1	
Mn	307	619	
Mo	2	3	
Ni	7	13	
Pb	49	192	
Zn	330	1150	
B	16	34	
S	1594	3157	
pH (water)	6.5	6.4	7.1

* TKN = total Kjeldahl nitrogen; ** Mg - S concentrations all reported in mg/l.

The amount of cadmium contamination in experiments is assumed, on the basis of the CSIR analyses, to be negligible, providing that Cd concentrations have not greatly increased since the previous analyses.

3.3 Methods

3.3.1 Particle size distribution

The compost was first air dried at room temperature, and then dry sieved into size fractions of > 2, 2-1, 1-0.1, and < 0.1 mm by shaking through a nest of sieves. Another size fraction, the < 2 mm size fraction, was obtained by sieving the bulk compost through a 2 mm sieve. The moisture content of each of the size fractions was determined by measuring the mass loss after oven-drying small samples at 110 °C for 24 hours.

3.3.2 Specific surface area

The extent of adsorption taking place on a solid is directly related to the surface area of that solid. The particle surface area of the compost samples of each of the size fractions < 2, 2-1, 1-0.1, and < 0.1 mm, was determined using a Micrometrics ASAP 2000 instrument (Department of Chemical Engineering, University of Cape Town), by the Brunauer, Emmett, and Teller method, using nitrogen (N₂) as the adsorbing gas (Carter *et al.*, 1986). This method makes use of the BET equation which is derived from multimolecular adsorption theory and provides for the number of adsorbate molecules in a monolayer (Appendix 1 provides a more comprehensive description of the BET equation). The Micrometrics ASAP 2000 instrument and BET equation are used to determine the volume of gas adsorbed in a monolayer on the surface of the compost. Since the cross sectional area occupied by a N₂ molecule is known, the surface area can be computed.

3.3.3 Cation exchange capacity (CEC)

The cation exchange capacity of the four size fractions (< 2, 2-1, 1-0.1, and < 0.1), was determined using the Gillman method (Rhoades, 1992). Using this method, 2 g of air dried compost was equilibrated with 0.1 M BaCl₂ saturating solution which was then decanted. The compost was then equilibrated with an MgSO₄ solution. The supernatant was then decanted, filtered through a 0.45 µm millipore filter, and analyzed for Mg by flame atomic absorption spectroscopy (AAS). The atomic absorption instrument was a Varian AA 30 spectrometer, and magnesium was determined with an air-acetylene flame, at 202.5 nm, with background correction. No ionization suppressant was required. The amount of Mg

adsorbed was then calculated from the difference in the Mg concentrations before and after adsorption. The pH of the suspensions was recorded using a Metrohm 691 pH meter. The experiment was performed in duplicate. A more detailed description of this method is given in Appendix 2.

3.3.4 Potentiometric titration

Cation exchangers which are fully protonated can be considered as insoluble acids since, in many respects, they act like their soluble counterparts, for example, they can be titrated with standard bases (Helfferich, 1962). In such a titration the ion exchanger remains insoluble but equilibrates with the solution to which the titrant is added. The neutralization of the exchanger can be observed by recording the pH of the supernatant solution while the titration is in progress.

A potentiometric titration of the compost was done in order to determine several properties of the compost, particularly the pK values of acidic groups and total acidity. The effect on the shape of the titration curve of ionic strength and equilibration time of the compost with added base or acid, was also determined.

The experiment was performed by two methods :

- i) A serial titration : Samples of compost, weighing 1 g (dry mass) of the < 2 mm size fraction were measured into 50 ml centrifuge tubes. To these samples were added varying volumes, up to 30 ml, of 0.01 M HCl or NaOH which were prepared in 0.1 M NaCl to ensure constant ionic strength. The volume of solution in each of the centrifuge tubes was then made up to 30 ml, as necessary, with 0.1 M NaCl solution (i.e. ionic strength (I) = 0.1). The suspensions were allowed to equilibrate on a reciprocal shaker overnight. The pH of each of the suspensions was then measured using a Metrohm 691 pH meter. The experiment was performed in duplicate.
- ii) This experiment was conducted in a similar manner to experiment (i) above, except that equilibration time was shorter (30 minutes), and no background electrolyte was added (I = 0). Duplicates were not made, since the high reproducibility of the method was known from the results of the duplicate analyses obtained from experiment (i).

3.4 Results and discussion

3.4.1 Compost characterization

The results for particle size distribution, cation exchange capacity, and specific surface area studies are tabulated in Table 3.2.

Table 3.2 : Experimental results for CEC, specific surface area, and particle size distribution determinations.

Particle size (mm)	Distribution (%)	BET specific surface area (m ² /g)	CEC		
			pH	Mean (mmol _c /kg)	RSD (%)
> 2	33				
< 2	67	0.85	7.65	113	0.0
1-2	14	0.83	6.57	99.8	3.9
0.1-1	52	0.68	7.61	115	0.7
< 0.1	1	1.83	7.16	299	0.1

The CECs determined are low compared to the CEC estimation of other humic substances. McBride (1994) states that, as a general rule, each weight percent of organic matter in soils contributes approximately 30 mmol_c/kg to the **total CEC of the soil**. Horacek *et al.* (1994) also found the CEC of peat from West Bohemia to be approximately 3500 mmol_c/kg. Organic matter in soils and peat is, however, typically decomposed to a larger extent than the compost due to a longer decomposition time, resulting in smaller particle sizes with a higher specific surface area and a higher concentration of acidic functional groups. Since the CEC is related to the surface area and charge (which in turn are related to particle size, and the concentration and dissociation constants of the acidic functional groups, respectively) of the material (Tan, 1994), it is therefore not surprising that the CEC of the compost is low. Furthermore, Horacek *et al.* (1994) used far higher equilibrium concentrations of counter ion (32.5 mmol_c Ca²⁺/l, as opposed to 2.5 mmol_c Mg²⁺/l) which may also have contributed to the large CEC discrepancy between peat-like materials and the composted sewage sludge.

It should also be noted that the cation exchange capacity is largely dependent on pH since the degree of ionization of acidic functional groups responsible for the ion exchange also is largely pH dependent (Helfferich, 1962; Sposito, 1989; Stumm, 1981). Using the Gouy-Chapman double layer model, it has been shown that CEC increases as ionic strength decreases and becomes equal to the total surface charge at infinite dilution (van Olphen, 1977). Thus CEC measurements are also highly subject to the conditions under which they are measured, and can only be realistically compared to experiments in which the conditions are similar.

3.4.2 Potentiometric titration

The results of experiments (i) and (ii) are presented Figure 3.1 (original data are reported in Appendix 3). The very low RSD values for the duplicate samples of experiment (i) indicate that the results and thus the method is highly reproducible. Therefore, as previously mentioned, duplicate samples were not performed for the second experiment.

There is a considerable difference in the shape of the two titration curves in Figure 3.1. The different experimental conditions used when obtaining these curves, namely background electrolyte concentrations and equilibration time, may account for the differences. The titration curve for experiment (i) is straighter, has slightly higher pHs after equivalent additions of titrant at low pH, and significantly lower pHs after equivalent additions of titrant at high pH, than indicated by the titration curve obtained from experiment (ii).

Background electrolyte effects

The background electrolyte concentration has little effect on the titration curves of dissolved acids and bases, but it does change the titration curves of suspended ion exchange resins (Helfferich, 1962). When an acidic ion-exchange solid in the H^+ form is placed in a solution of NaCl, the ion exchange begins even before the NaOH is added, and the solution becomes acidic. The pH attained by the solution at this stage depends on the amount of NaCl added, the ratio of solution to ion exchange material weight, and the ion exchange capacity. With addition of NaOH, the solution is progressively neutralized and, at the same time, the ion exchange is driven to completion. The titration curve thus shows a gradual rise in the early stages of the titration, and a steep rise at the point of complete neutralization. The presence of the salt results in a lower and slightly more sloping curve in the early titration stages. Otherwise the curve should remain

unchanged. Figure 3.1 illustrates that this has not been the case with the compost. The initial slope of the titration curve for experiment (i) is not steeper, nor is it at a lower pH than that of experiment (ii). The curve is also much straighter and the steps are hardly visible. The cause of this behaviour may thus be related to the equilibration time.

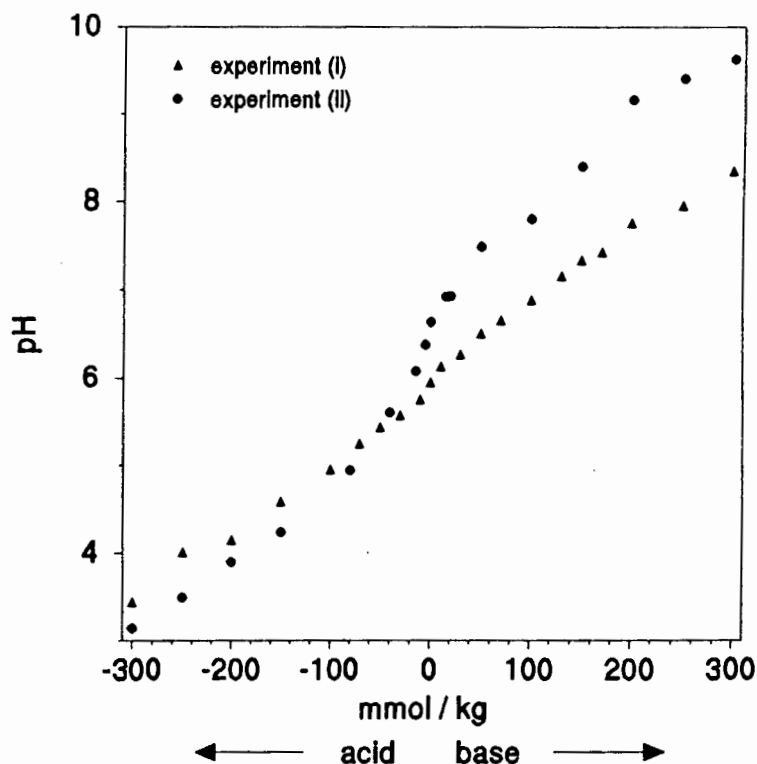


Figure 3.1 : Potentiometric titration curves obtained for experiments (i) and (ii).
 Experiment (i) : $I = 0.1$; equilibration time = overnight.
 Experiment (ii) : $I = 0$; equilibration time = 30 minutes.

Equilibration time

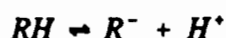
Several researchers have reported a similar, pronounced tendency for pH values to decrease with time in alkaline solutions (Dempsey and O'Melia, 1983; Fliag *et al.*, 1975). A proposed, but speculative, reason for the observed pH decrease is that in the presence of oxygen, both chemical and bacterially mediated oxidation reactions occur, producing acids (Swift and Posner, 1972). Borggaard (1974) has also found that alkaline solutions of humic substances are stable only under nitrogen and in sterile, sealed ampoules. In addition, it is believed that base catalyzed hydrolysis of esters and peptides release additional carboxylic acids (Martin and Reeve, 1958). The increase in concentration of acids may have caused the general decrease in pH, particularly at high pH (as is noted in Figure 3.1), and

a flattening of the titration curve, possibly due to the formation of a wider range of acidic functional groups with a wide range of pK values.

Alternatively, the smoothing and depression of the pH titration curve at longer equilibration time may be explained by kinetics. There may be significant number of acidic functional groups which require a longer equilibration time causing the observed depression of the titration curve in experiment (i). The smoothing of the curve relative to that obtained for the short equilibration time may be caused by the subsequent equilibration of acidic groups with a wider range of pK values. However, Virararghavan and Dronamraju (1993) found that equilibration time for peat, although under a different set of conditions, was two hours, with 90 % of equilibration taking place in the first 30 minutes. Thus kinetic factors are unlikely to be the cause of the difference in shape between the titration curves obtained for both experiments.

Titration curve shape and pK values

The pK value of an acidic group RH can be defined as the negative logarithm of the dissociation constant, K, for the reaction



where K is defined as

$$K = \frac{[R^-][H^+]}{[RH]}$$

Thus the lower the pK of an acid, the higher is its acidity. The pK can be shown to be equivalent to the pH at which 50 % of the acid is in the dissociated form, and can be determined from the titration curves as the pH at the inflection point of the step in the curve.

The titration curve obtained from experiment (ii) (Figure 3.1) is not unlike that of a polyfunctional group cation exchanger (Helfferich, 1962), and seems to indicate the presence of both strong and weak acid groups, giving two distinct steps in the titration curve with inflection points at approximately pH 6.3 and 8.4. Hence the pK values of these acidic groups is approximately 6.3 and 8.4. The degree of ionization of the acidic groups depends

on their pK values and the pH. Acidic groups become predominantly nonionic when the pH drops below the pK value of the groups, resulting in a marked decrease in CEC.

Polyfunctional ion exchangers (such as compost) contain ionogenic groups which differ in their pK values. Here, the various effects produced by the different groups are superimposed on one another (Perdue, 1985). Humic substances contain acidic functional groups such as carboxylic acids, phenols, ammonium ions, alcohols and thiols. The acidity (pK) of an ionizable functional group greatly depends on its electrostatic environment (the spatial distribution of proximate dipolar groups). The functional group acidity also depends on delocalisation effects. The delocalisation of electron density in the conjugate base of an acid enhances its acidity, as indicated by the relative acidities of alcohols and carboxylic acids. While O-H bonds are heterolytically broken in both cases, only carboxylic acids yield delocalised electrons, explaining their greater relative acidity (pK~2-7 for carboxylic groups, and pK~8-11 for phenolic groups) (Perdue, 1985). The overall result of electrostatic and delocalization effects on the acidities of organic acids can be illustrated by the frequency histogram in Figure 3.2 (Perdue, 1985).

Figure 3.2 represents the pK values for all the simple organic acids containing only C, O, and H (Christensen *et al.*, 1976; Martell and Smith, 1977). It is apparent from Figure 3.2 that the frequency of occurrence of the carboxylic acid groups has an approximately Gaussian distribution with a mean pK value of about 4.5. The phenolic groups are similarly distributed around a mean pK value of approximately 10.

Since the compost is humified, and humic materials contain predominantly carboxylic and phenolic functional groups (Perdue, 1985), the pK values of 6.3 and 8.4 are most likely associated with these groups, respectively. These values differ somewhat from the mean pK values indicated in Figure 3.2. This discrepancy can be attributed to several factors :

a) The pK values reported by Christensen *et al.* (1976) and Martell and Smith (1977) are of synthetically produced carboxylic and phenolic groups which are far simpler and contain fewer protons per molecule than those of humic acids. Probability based models predict that the successive removal of protons from a single molecule becomes increasingly unlikely because of a build-up of negative charge on the molecule (McBride, 1994). Since humic acids are predominantly polyprotic acids, the pKs of their acidic groups would be expected to be higher on average, than those of synthetic, small molecular weight,

organic acids. This phenomenon may explain the higher than reported pK value of the carboxylic groups, but not of the phenolic groups, since these pK values are somewhat lower than the reported average values in Figure 3.2.

b) It is possible, that the mean distribution of pK values of carboxylic acid and phenolic groups on the compost are different to the mean values reported by Perdue (1985) in Figure 3.2.

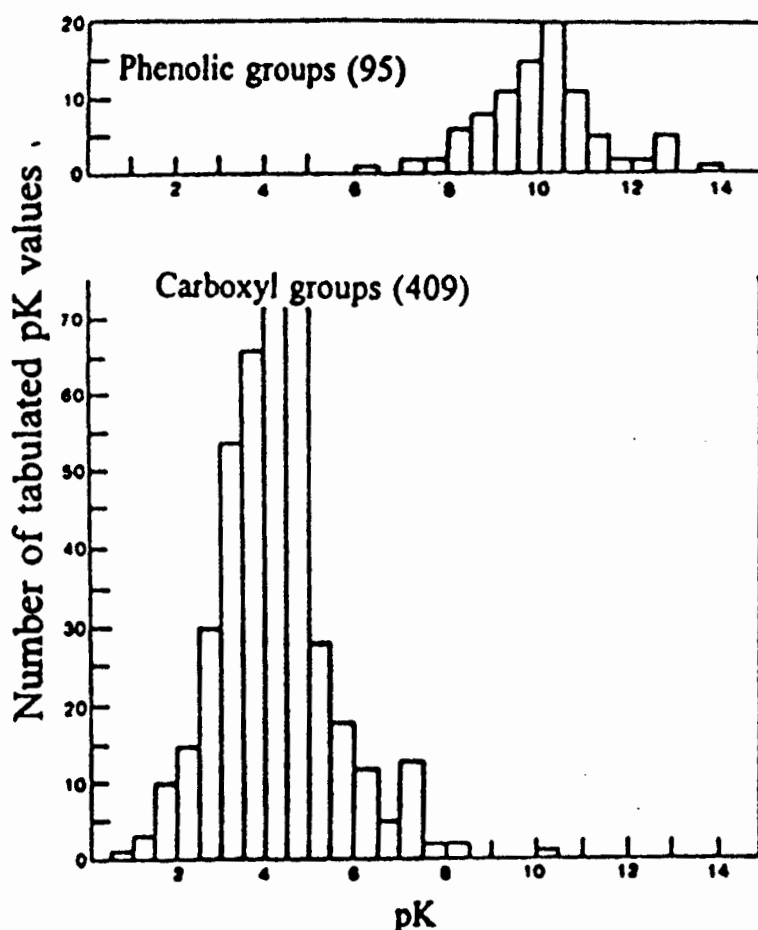


Figure 3.2 : Distribution of pK values in simple organic acids (After Perdue, 1985).

Total acidity

The total acidity includes all acidic protons in the humic substance which, in this case, are predominantly carboxylic and phenolic protons. From the titration curve of experiment (ii), the amount of base consumed at the maximum addition of base, can be calculated, and is equivalent to the total acidity. The pH, after addition of 30 ml 0.01 M NaOH (or 300 mmol OH^- / kg) was 9.6 (or 1.19 mmol OH^- / kg). Thus the total acidity of the compost is approximately 298 mmol OH^- / kg. The titration curve of experiment (i) cannot be used for this determination since base catalyzed hydrolysis and oxidation reactions which may

have occurred in the compost would serve to alter the number of acidic groups (discussed previously in this section). These reactions may also have occurred in the titration in experiment (ii), but because of the short time period before pH was measured, it is assumed that the extent of these reactions was small enough so as to not significantly alter the number of acid groups.

The total acidity can be equated to the potential cation exchange capacity if all acidic functional groups partake in cation adsorption. The total acidity measured in this experiment is approximately three times the CEC determined in the experiment in which CEC was measured using the Gillman method (Section 3.3.3).

Possible effect of compost pretreatment

The compost was not pre-treated prior to use in the above experiments. However, the analyses of the compost, the results of which are presented and have been discussed in Section 3.2, indicate that there are high concentrations of base cations in the compost (Table 3.1). It is not known in which form the cations are present. The maximum number of equivalents of charge which could be contributed by the major base cations (Ca^{2+} , K^+ , $\text{Fe}^{2+/3+}$, Mn^{2+} , and Zn^{2+}) if they were all available for complexation by the compost, and if the analyses are an accurate reflection of the composition of the samples studied, is 679 mmol_e / kg. It is likely that a small proportion of this sum is responsible for occupying many of the humic acid functional group exchange sites. This is demonstrated by the fact that if all the acidic groups were in the H^+ form, then only base addition would have been necessary to obtain the above titration curves, and the addition of HCl would have resulted in a sharper decrease in pH. Hence the total acidity and pK values should be considered as purely empirically determined properties of untreated compost.

Another approach to this experiment may have been to pretreat the compost by converting all the acidic functional groups to the H^+ form by washing it with large volumes of dilute acids, followed by a base titration; or by converting all the acidic functional groups to the K^+ form by treating with KOH, and the back-titrating with acid. However, since part of the aim of this work was to assess the potential for the use of this compost as an inexpensive biosorbent, it was used in the form in which it may be foreseen to be used, if it possesses those properties which would make it suitable as a biosorbent.

3.5 Discussion and conclusions

In this study, preliminary investigations suggested that properties such as surface area and cation exchange capacity (CEC) do not vary sufficiently with particle size to warrant a distinction based on particle size beyond separating the > 2 mm fraction, which consisted predominantly of wood chips. Also the greater homogeneity of the < 2 mm size fraction enabled further experiments to be performed in a reproducible manner whilst using small sample sizes.

The cation exchange capacity is lower than might have been expected (McBride, 1994; Horacek, 1994). However, as suggested previously, the CEC measured may not be the maximum attainable CEC, and a recommendation for future work on the compost would be the determination of CEC using an adsorption isotherm approach which may be more appropriate in determining a CEC value which is operationally meaningful.

A marked change in some of the properties of compost suspensions with time, and under certain conditions, was noted. The most marked property change was that suspected of being caused by long-term exposure of an aqueous suspension of compost to air, causing oxidation reactions which lowered the pH of the medium in which the compost was suspended. The change in properties of the compost and the aqueous medium in which it was suspended are difficult to quantify and sensitive work should thus be conducted under nitrogen gas.

The pK values obtained from the titration curve of experiment (ii), and which are assumed to be attributable to the carboxylic acid and phenolic groups, are comparable to several of those obtained from the literature. Commonly, in a potentiometric titration, the curve obtained has one broad step for humic materials (Marinsky and Ephraim, 1986; Stevenson, 1976a). Marinsky and Ephraim (1986) found pK values of different fulvic acids to fall in the range of 7-7.5. Stevenson (1976b), however, reports pK values of 4.82 and 4.86 for soil and peat humic acids, respectively. These measurements were, however, conducted at I (ionic strength) = 0.1, whereas the pK values of the acidic groups in the compost were determined at $I = 0$. Posner (1964) found that pK values of humic acids increase with decreasing I . This may explain the relatively low pK values obtained by Stevenson (1976b).

The mean pK of the carboxylic acid groups (approximately 6.3), obtained from the potentiometric titration, is useful information in that it indicates the minimum pH at which significant CEC of the material exists. Since the CEC measurements made using the Gillman method were made well above pH 6.3, the effect of pH on CEC is regarded as negligible.

4. Cadmium adsorption by composted sewage sludge

4.1 Introduction

The potential of composted sewage sludge as a biosorbent for the treatment of heavy metal contaminated effluents is studied in this chapter. Since Cd is one of the three most ubiquitous and toxic heavy metals in the environment and occurs in a wide range of wastewaters, it was chosen as a representative of heavy metals for the purposes of this study. Current regulations prohibit waste water effluents containing Cd concentrations higher than a specified limit from being discharged. The current limit in South Africa is a combined total metals concentration of Cd + As + Hg of less than 2 mg/l (John Stowe, Cape Town Scientific Services, telephonic communication).

The experiments described in this chapter not only provide valuable information as to the nature of compost as a biosorbent, but also insight into more fundamental scientific principles. Hence, many of the interpretations of the results concentrate as much on the processes which influence Cd adsorption as on the qualification of compost as a biosorbent.

It is important to note that industrial effluents are often more complex than the systems under consideration in this study. In addition to the possibility of a range of heavy metals being present in the effluent, the ionic strength and the nature of competing ligands (inorganic and soluble organic anions which may complex the heavy metals) and cations (which could compete for adsorption sites on the compost) may vary dramatically from one effluent to another. Many of the experiments performed, and their interpretations, are largely empirical, are not directly comparable to other published results, and cannot necessarily be extrapolated to yield information outside of the range of conditions under which the experiments were performed.

4.2 Theory

Many studies have used similar theory and models to those applied in this chapter. Although the theoretical treatment of the experimental data obtained from experiments in this study is not extensive, it is, however, appropriate, before discussing the experiments conducted in this study, to describe some of the relevant theory to clarify notation and concepts.

4.2.1 Adsorption

Several approaches have been used to describe and model adsorption reactions. The most common of these is the adsorption isotherm approach, where the total concentration of adsorbed species i (q_i) is modelled as a function of the equilibrium solution concentration of the species (c) at constant temperature and pressure. This type of data can be fitted to an adsorption isotherm such as the Langmuir or Freundlich isotherms. This approach gives valuable insight into the capacity of a surface to retain a chemical species under specified conditions.

Four categories of adsorption isotherm may be recognised (Sposito, 1989) : the S, H, L, and C-curve isotherms. Adsorption isotherms describing the adsorption of heavy metals by organic matter are typically of the L-curve isotherm type which is characterized by a steep initial slope that does not increase with the concentration of adsorbing species in solution. This characteristic results from a high relative affinity of the adsorbent for the adsorbing species at low surface coverage, coupled with a decreasing amount of adsorbing surface remaining as the surface excess of the adsorbate increases. In contrast, the S-curve isotherm is characterised by an initially small slope that increases with adsorbing species concentration. This behaviour suggests that the affinity between the adsorbent and the adsorbing species is less than that between the aqueous solution and the adsorbing species. The C-curve isotherm is characterised by an initial slope that remains independent of adsorbing species concentration until maximum adsorption is achieved.

The L-curve isotherm is usually described by the Langmuir equation or the Freundlich equation (Sposito, 1989). The Langmuir equation has the form :

$$\frac{1}{q_i} = \frac{1}{bKc_i} + \frac{1}{b}$$

where b and K are adjustable parameters. The parameter b represents the value of q_i that is approached asymptotically as c_i becomes arbitrarily large. The parameter K determines the magnitude of the initial slope of the isotherm, and is also a measure of the bond strength holding the adsorbed solute on the adsorbent surface (Travis and Etnier, 1981).

Thus a plot of $1/q_i$ against $1/c_i$ should be a straight line with slope equal to $1/bK$, and a y intercept of $1/b$ if the Langmuir equation is applicable. A limitation of the Freundlich isotherm, relative to the Langmuir isotherm, is that it does not imply a maximum quantity of adsorption.

Adsorption isotherm equations cannot be used to identify the operation of adsorption mechanisms, and do not distinguish between adsorption and precipitation. Adsorption isotherm equations are therefore regarded as curve-fitting models without particular molecular significance, but with predictive and comparative utility.

4.2.2 pH effects on Cd adsorption

As pH increases, the adsorption of metal cations from solution by humic materials is enhanced (Stumm, 1992). This effect is principally the result of increases in the net negative charge on the material surface, caused by the dissociation of acidic functional groups, which in turn increases the electrostatic attraction of the surface for metal cations. These acidic groups are predominantly carboxylic acid and phenolic groups which are easily dissociated as pH increases (Section 3.4.2). The exchange reaction can be written as



clearly illustrating the direct effect of pH on the direction of the metal adsorption / desorption equilibrium.

If humic materials are reacted with a series of aqueous solutions of increasing pH, containing a metal cation at the same initial concentration, the amount of metal cation adsorbed will increase with pH, unless ligands in the solution compete overwhelmingly with the surface functional groups for the metal (Sposito, 1989). In the absence of significant ligand competition, a graph of metal cation adsorbed (q_M) versus pH will have a characteristic sigmoidal shape known as an adsorption edge (Sposito, 1989). These curves are often characterized by the value of pH_{50} , the pH value at which half of the maximum value of q_M is achieved. Values of pH_{50} usually have a negative correlation with the relative affinity of an adsorbent for a metal cation (Sposito, 1989).

Hydrolysis of the form



is thought to enhance metal cation adsorption (Sposito, 1989). The value of pH_{50} is nearly always well below the pH value at which significant hydrolysis occurs in aqueous solution. However, Sposito (1989) suggests that it is possible for hydrolysed species (eg. $MOH^{(m-1)+}$ in the above equation) to be adsorbed strongly because they are desolvated more easily than free metal cations, and contribute to the rapid increase of q_M near pH_{50} . Sposito (1989) also suggests that low concentrations of hydrolytic species will not suppress this effect since the complexes can be produced via the equation given above until the supply of free metal cation is depleted.

4.2.3 Speciation in solution

Speciation and ionic strength can greatly affect cation adsorption phenomena. Anionic ligand competition for the adsorbing cation, and competition effects for adsorption sites between different cationic species can result in significant decreases in metal cation adsorption (Bourg, 1988).

The speciation of Cd in aqueous systems has largely been discussed in Chapter 1. Ionic strength (I), pH and redox potential (pE) are the three major parameters which are commonly recognized to influence speciation (Ritchie and Sposito, 1995). Reaction kinetics and the relative concentrations and affinities of cations and anions may be equally important.

Chemical speciation is often studied using analytical methods. An alternative approach involves the application of theoretical chemical concepts to predict the distribution and transformation of chemical species. Many geochemical models have been developed to solve problems involving chemical equilibria (speciation), one of the most commonly used being MINTEQA2 (Allison *et al.*, 1991), which is based on equilibrium thermodynamics. MINTEQA2 calculates the equilibrium composition of dilute aqueous systems with reference to soluble, solid, adsorbed, and gas phases, taking into account varying conditions such as pH, ionic strength, temperature and redox status. The MINTEQA2 package also includes an extensive database comprising thermodynamic data for soluble complexes,

mineral solubilities, gas solubilities, and redox couples.

The accuracy of speciation predictions by MINTEQA2 is limited by the reliability and quality of the database from which the calculations are made. Uncertainties in the mathematical formulation of existing processes (e.g. uncertainty in the determination of activity coefficients at high ionic strength, or if the stability constant of an important complex is unknown) may be reflected by poor reliability of the calculated results. Kinetic considerations are also not taken into account in this model, and if a chemical reaction cannot occur, or progresses very slowly for kinetic reasons, the speciation results may not be sufficiently representative of reality (Bourg, 1988).

4.2.4 Conditional stability constants and complexation capacities

Conditional stability constants (K_c), instead of normal stability constants are used to characterise metal binding by a multi-ligand mixture such as compost and other humic substances. The reason for this is that humic substances have a multi-ligand nature, the individual components and side reactions of which are unknown. Unlike stability constants, which are a function of ionic strength only, conditional stability constants are a function of ionic strength, pH and concentrations of competing metal ions and ligands (Perdue, 1989). The expression describing a conditional stability constant has the form

$$K_c = \frac{[M_B]}{[M_F][L_F]}$$

where $[M_B]$ is the sum of the concentrations of all the complexes formed between the metal cation (M) and the ligand (L), $[L_F]$ is the sum of the concentrations of all the binding sites that are not associated with M, and $[M_F]$ is the sum of metal species that are not associated with the multi-ligand mixture (Perdue, 1989).

If a ligand is titrated with increasing amounts of metal, using an appropriate technique for the differentiation of the free metal concentration, $[M_F]$, from that of the bound or complexed metal, $[M_B]$, then values for the conditional stability constant K_c , and the total ligand concentration, L' (hence complexation capacity), may be obtained from the graphical solution of the following linear relationship (Ruzic, 1982) :

$$\frac{[M_F]}{[M_B]} = \frac{[M_F]}{[L']} + \frac{1}{K_c [L']}$$

where the conditional stability constant and complexation capacity can be obtained from the intercept and slope respectively. Note that this equation applies only to those complexes possessing 1 : 1 stoichiometry.

4.3 Materials and methods

4.3.1 pH effects on Cd adsorption

Samples of compost (0.47 g dry mass) of the < 2 mm size fraction were weighed out into four sets of 11 centrifuge tubes. Aliquots ranging between 0 and 25 ml of either 0.01 M NaOH or 0.01 M HCl made up in 0.1 M NaCl were then added to each set of centrifuge tubes, and made up to 25 ml with 0.1 M NaCl solution as necessary. The centrifuge tubes were then stoppered and placed in a reciprocal shaker for 25 hours, after which the pH of the suspensions was measured. The volume of solution in each centrifuge tube was further increased to 30 ml using a CdSO₄-0.1 M NaCl solution so that the initial concentrations of Cd were 2.10, 4.98, and 9.97 mg/l (or 134, 317, and 636 mg Cd/kg compost respectively). These Cd-amended compost suspensions were then equilibrated in the reciprocal shaker for a further 27 hours, after which they were centrifuged and their supernatant pH measured. Samples of each suspension were then filtered through 0.45 µm millipore filters and analyzed for Cd by flame atomic absorption spectrometry (AAS) using a Varian AA 30 spectrometer with an air-acetylene flame, and measuring absorbance at 228.8 nm with background correction. Three absorbance readings of each sample were taken, typically with RSD values lower than 1.5%.

4.3.2 Adsorption isotherms

Small samples of compost (1.40 g dry mass) of the < 2 mm size fraction were placed in seven sets of 1-litre plastic bottles, and varying amounts of CdSO₄ solution (100 mg/l), in addition to a volume of distilled water, were added to make the volume in each bottle up to 895 ml. pH was brought to within 6.8-7.2 by adding 15 ml of 0.01 M NaOH in order to optimize adsorption and minimise oxidation (so that small changes in pH would not result

in significant changes in q_{Cd} , and would not promote excessive oxidation or base catalyzed hydrolysis reactions). Total solution volume in the experiments was thus 910ml. NaCl, Na_2SO_4 , and $CaCl_2$ were used as background electrolytes and were made up in different concentrations. The electrolyte concentrations (Molar) used were 0.005, 0.05 (duplicate), 0.5 (NaCl); 0.025 and 0.0167 (Na_2SO_4); and 0.025 and 0.0167 ($CaCl_2$).

The above-mentioned concentrations of background electrolyte were selected for several purposes :

- 1) To assess the effect of changing the concentration of a single electrolyte on the adsorption isotherm.
- 2) To assess the effect of different background electrolytes on the adsorption of Cd at a constant ionic strength (I) such that the activity of Cd would be constant. The selected ionic strength for the study was 0.05 M. The concentrations of background electrolyte required to achieve this ionic strength were calculated using the following relationship:

$$I = \frac{1}{2} \sum_i (m_i z_i^2)$$

where m_i = concentration of ionic species i, and z_i = charge of ionic species i. The products of m_i and z_i^2 are summed over all ionic species in solution assuming that no speciation of the ionic constituents occurs. Using this approach, background electrolyte concentrations for this study were determined as 0.05 M NaCl, 0.0167 M Na_2SO_4 and 0.0167 M $CaCl_2$.

- 3) To assess the separate effects of background anionic and cationic species on Cd adsorption. Background electrolyte concentrations were selected such that each solution contained the same number of equivalents of background cations and anions. The concentrations selected were 0.05 M NaCl, 0.025 M Na_2SO_4 and 0.025 M $CaCl_2$.

The plastic bottles were sealed, placed in a reciprocal shaker, and allowed to equilibrate overnight. The pH and electrical conductivity (EC) of each of the solutions was then measured to confirm that background conditions both within and between experiments were not significantly different. In this way, differences in Cd adsorption for reasons other than the concentration and nature of the background electrolyte could be eliminated. Samples from each of the suspensions were then taken and filtered through 0.45 μm millipore filters. These were analyzed for Cd by AAS (Section 4.3.1). The amount of Cd adsorbed per kilogram of compost (q_i) was then calculated and plotted against c_i to construct adsorption

isotherms.

4.3.3 Conditional stability constants and complexation capacities

Conditional stability constants (K_c) and complexation capacities of the compost with respect to Cd adsorption, under the conditions described in section 4.3.2, were calculated by plotting $[Cd_F]/[Cd_B]$ against $[Cd_F]$. Background electrolyte concentrations of 0.005 M and 0.05 M NaCl, 0.0167 M and 0.025 M Na_2SO_4 and 0.0167 M $CaCl_2$ were used. Regression curves were fitted to these plots, and the conditional stability constants and complexation capacities were estimated from the intercept and slope, respectively. Complexation capacities were also estimated from another mathematical model, the Langmuir equation, where regression of $1/q_{Cd}$ against $1/c_{Cd}$ yielded a straight line with y intercept $1/b$, where b is the predicted complexation capacity.

4.3.4 Column experiments

4.3.4.1 Column reproducibility tests

Samples of dry compost (4.25 g; < 2 mm size fraction) were placed in small plastic columns of internal diameter 15.6 mm and length 5 cm, and the contents of each column was saturated with distilled water. A 0.01 M solution of NaOH (pH 12.07) was passed through the column at a constant flow rate of 69.4 ml/hr using a peristaltic pump. A Gilson fraction collector was used to take samples of the effluent at specified time intervals. The pH of these samples was then measured by using a Metrohm 691 pH meter, and breakthrough curves of pH against volume passed through the column were determined for each column. This experiment was repeated three times and the results compared for reproducibility (data from experiments tabulated in Table A7.1).

Reproducibility of the column experiments is important because only a small sample (6.5g) of compost was used in the column experiment involving Cd. The reproducibility test was designed to be simple, fast, and as similar to the Cd experiment as possible. pH measurement was a simple procedure, and breakthrough time, relative to that when Cd is passed through the column, was fast.

4.3.4.2 Cadmium adsorption

A Cd solution (5.54 mg/l; pH 7.08) in 0.05 M NaCl was passed at a flow rate of 80 ml/hr through a column of internal diameter 15.6 mm, length 54 mm and volume 10.32 cm³. The column contained 6 g of dry compost of size fraction < 2 mm.

Constant flow rates were regulated by means of a peristaltic pump, and an autosampler was used to collect effluent samples for a specified duration at specified time intervals (Appendix 8, Table A8.1). The samples were subsequently analyzed for Cd using AAS (Section 4.3.1), and the concentrations of Cd were plotted as a function of the volume of eluent which had passed through the column.

4.3.4.3 Cadmium desorption from column

After the Cd solution had been passed through the column for 71 hours, a solution containing only 0.05 mol/l NaCl was run through the column for several hours to assess the extent and ease of Cd desorption from the compost. Samples were taken at specified time intervals (Appendix 8, Table A8.2) and analyzed for Cd using AAS (Section 4.3.1).

4.3.5 Desorption experiments

4.3.5.1 Preliminary adsorption

Compost samples of 1.40 g were added to 910 ml solutions which were made up by adding 15 ml 0.01 M NaOH and varying volumes of distilled water and 100 mg/l Cd solution. Salts of NaCl and Na₂SO₄ were added as background electrolytes at concentrations of 0.05 and 0.025 M, respectively. Initial concentrations of Cd were 11 mg/l in the NaCl solutions, and 16.5 mg/l in the Na₂SO₄ solutions. Duplicates of each compost suspension were made. The suspensions were allowed to equilibrate overnight in a reciprocal shaker, after which samples were withdrawn, filtered through 0.45 µm millipore filters and analyzed for Cd by AAS (Section 4.3.1).

4.3.5.2 Desorption

The compost was recovered by filtration, and the mass of recovered compost plus entrained solution was determined. The recovered compost was placed in 50 ml centrifuge tubes. To one of each of the duplicate samples 25 ml 0.05 M H₂SO₄ was added and to the other, 25 ml 0.1 M HCl was added. The resulting suspensions were equilibrated overnight and then

centrifuged. The supernatant was decanted, filtered through 0.45 μm millipore filters, and analyzed by AAS (Section 4.3.1). The mass of the compost and entrained solution was again determined. This procedure was repeated twice.

4.3.5.3 Adsorption after desorption

The recovered, treated compost was washed several times with distilled water and treated in the same way as described in Section 4.3.5.1 except that concentrated NaOH solution was used to adjust the pH of the solution to the desired range (Section 4.3.5.1).

4.4 Results and discussion

4.4.1 Adsorption edge

Experimental results of the column experiments conducted using different initial Cd concentrations are presented in Appendix 4 (Tables A4.1 to A4.3), and the adsorption edge plots of Cd adsorbed as a function of equilibrium pH are presented in Figure 4.1.

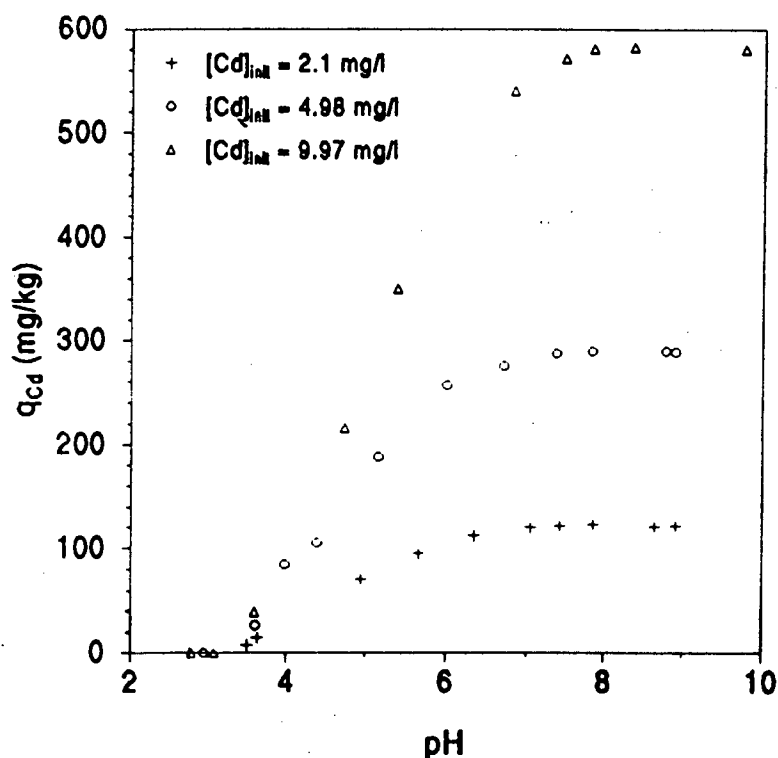


Figure 4.1 : Adsorption edges for Cd adsorption on composted sewage sludge at three different initial Cd concentrations, where the adsorbed phase cadmium concentration at equilibrium (q_{Cd}) is presented as a function of pH.

At low pH, very little Cd adsorption by the compost occurred, but as pH increased, so did the amount of Cd adsorbed (Figure 4.1). This trend of increasing q_{Cd} levelled off at pH values of approximately 7.5. The complexation capacity for Cd under each of the experimental conditions can be calculated by measuring q_{Cd} (max), the maximum amount of Cd which is adsorbed by the compost from each of the curves. Each of the curves are characterized numerically by their pH_{50} values which are tabulated along with the complexation capacities of the compost under each of the experimental conditions in Table 4.1.

Table 4.1 : Complexation capacities and pH_{50} values obtained from each of the experiments where different initial Cd concentrations were used.

$[Cd]_{initial}$ (mg/l)	pH_{50}	q_{Cd} (max) (mg/kg)
2.10	4.7	120
4.98	4.7	282
9.97	5.1	580

The pH_{50} values obtained for the curves are very similar to one another (RSD = 4 % between pH_{50} values). This is to be expected since it is the affinity of the material for an adsorbing species which determines the pH_{50} , and the initial solution-phase concentration of the adsorbing species should therefore not cause a change in the pH_{50} value. As discussed in Section 4.2.2, pH_{50} correlates negatively with the relative affinity of the adsorbent for the adsorbing metal cation species. However, different types of adsorbing sites with different affinities for heavy metals occur in humic substances, the stronger adsorbing sites occurring in smaller proportions (Gardiner, 1975). The strongly adsorbing sites may become fully saturated with Cd at low solution-phase Cd concentrations and at lower pH. Therefore pH_{50} may be expected to be slightly lower for solutions of low initial Cd concentration. The results in Table 4.1 suggest a slight increase in the adsorption edge pH_{50} value obtained when $[Cd]_{initial}$ was high (9.97 mg/l). This increase, however, is slight and not necessarily significant, and it is a matter of speculation as to whether the saturation of strongly adsorbing sites, or experimental error, is responsible for the slight, but observed

shift in the pH_{50} value.

4.4.1.1 Hydrolysis and adsorption

MINTEQA2 was used to describe the distribution of Cd species at an electrolyte concentration of 0.1 M NaCl and over the pH range investigated in this study. The results are presented in Table 4.2. Using initial exploratory runs, it was found that within the range of Cd : Cl ratio used in the different experiments, Cd-chloride speciation was independent of Cd concentration. This justified the use of an arbitrary, but realistic, Cd concentration of 5 mg/l in further modelling.

Table 4.2 : MINTEQA2 prediction of the distribution of Cd species in solution at varying pH, in a background electrolyte of 0.1 M NaCl and a Cd concentration of 5 mg/l.

Species	Distribution (%)			
	pH 10	pH 8.5	pH 7.5	pH 5
Cd^{2+}	7	17	19	19
$CdCl^+$	24	60	64	64
$CdCl_{2(aq)}$	6	15	16	16
$CdCl_3^-$			1	1
$CdOH^+$	2			
$CdOHCl_{(aq)}$	60	7		

From this species distribution, it is evident that up to pH 7.5, (at which maximum adsorption occurs) an insignificant proportion of Cd exists in the hydrolysed state. The mechanism of metal adsorption suggested by Sposito (1989) attributes increased adsorption with increasing pH to the formation of $CdOH^+$ complexes, which are more strongly bound because they have lower energies of desolvation. This mechanism, however, is unlikely for two reasons :

- 1) At any pH, a small proportion of Cd would exist as the $CdOH^+$ species. According to the mechanism proposed by Sposito (1989), low concentrations of this species would not suppress Cd adsorption and one would expect efficient removal of Cd from solution even at low pH values. However, in practice this is not observed (probably because at very low $CdOH^+$ concentrations the kinetics of the adsorption process are very slow) making the mechanism proposed by Sposito unlikely.

- 2) The CdOH^+ species has a smaller ionic potential relative to the Cd^{2+} species, resulting in a lower electrostatic attraction between CdOH^+ and the deprotonated functional groups on the compost.

There may, however, be merit in combining the mechanism suggested by Sposito with one which uses an increase in acidic functional group dissociation from the adsorbing surface to explain the increasing adsorption of Cd from solution with increasing pH. Such dissociation would increase the electrostatic attraction between Cd species and the surface, and would increase the capacity of the material to adsorb Cd. These two mechanisms may act synergistically to enable more Cd to be adsorbed at high pH than might be the case if both mechanisms were not acting simultaneously.

Removal of Cd from solution by precipitation as Cd hydroxide (McBride, 1994) is also not a feasible explanation for the decrease in equilibrium Cd concentration with increasing pH since the pH at which maximum adsorption occurs is lower than that at which a significant amount of $\text{Cd}(\text{OH})_2$ formation may be expected to occur (Section 1.5). The situation, however, is different for certain other metals such as copper, since the precipitation of $\text{Cu}(\text{OH})_2$ is initiated at much lower pH.

4.4.1.2 *pH changes after Cd equilibration*

The pH of the solutions after equilibration with Cd was observed to change markedly, particularly at high initial pH, where a significant decrease was noted. The pH values of the suspensions before and after equilibration with Cd are plotted in Figure 4.2. A tendency for the pH of the solutions to decrease after equilibration with the Cd solution is evident, particularly at high pH. Many other studies have found the same trend. Stevenson (1976a,b) and van Dijk (1971) observed a horizontal displacement of potentiometric titration curves for humic acids which was proportional to the amount of Cd added. They attributed this phenomenon to the release of otherwise non-titratable H^+ from the humic acid at low pH values and/or of protons from hydration water of the metal bound in 1 : 1 complexes at high pH values. Stevenson (1976b) observed this displacement over a range of Cd concentrations in pH 3 to 10 solutions of ionic strength 0.1 M. These experiments, however, were performed under nitrogen gas so that no chemically or bacterially mediated oxidation reactions (Section 3.4.2), which would lower the pH, could occur. However, in Figure 4.2

it is evident that the addition of the Cd solution results in a pH decrease only above pH values of approximately 6 to 7.5. Furthermore, comparison of the pH values after equilibrating with different initial concentrations of Cd (Figure 4.3) shows that there is no

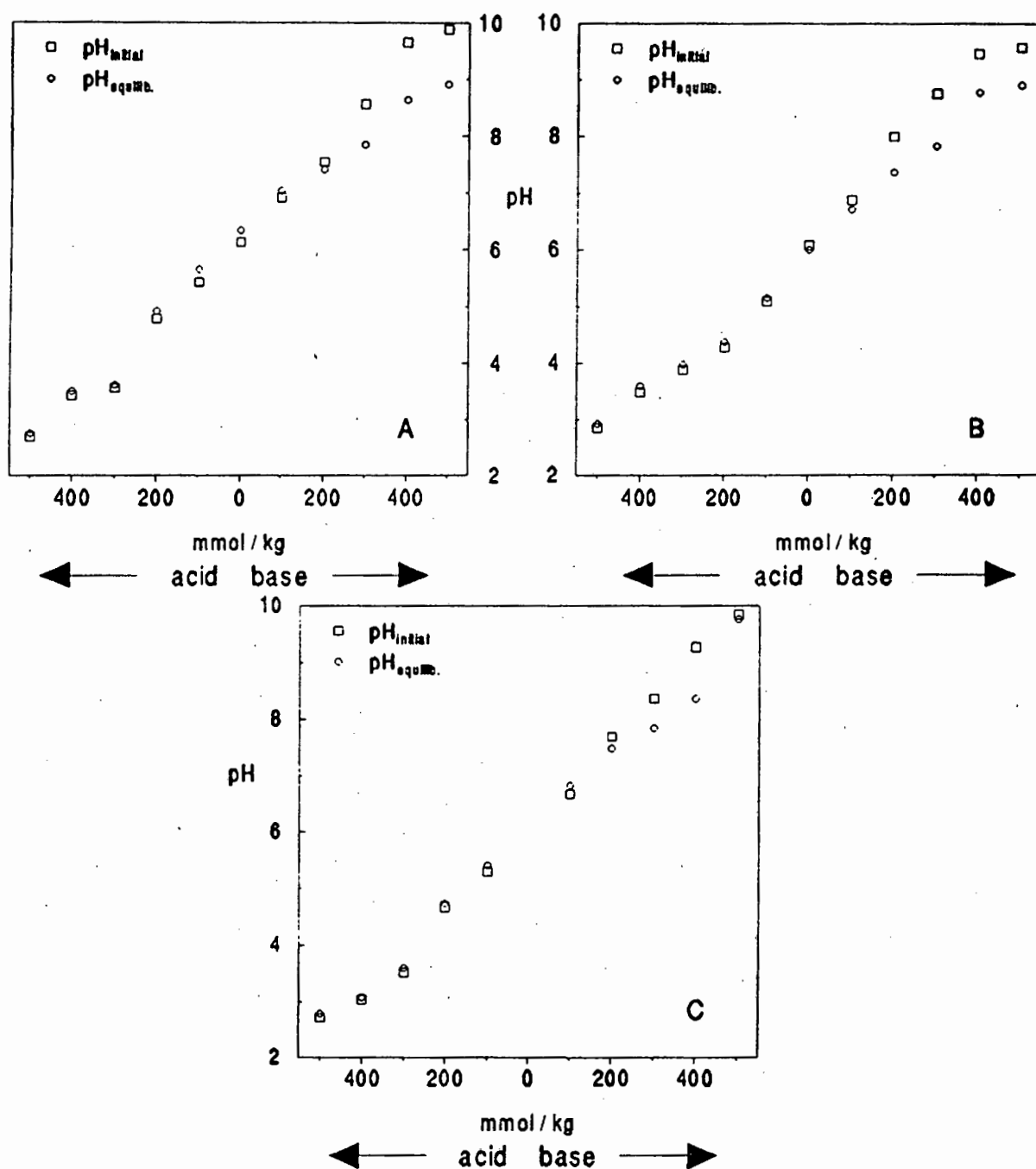


Figure 4.2 : pH values of Cd-amended compost suspensions before and after equilibration. Initial pH values of the suspensions were amended either with HCl or NaOH, and initial Cd concentrations were 2.10, 4.98 and 9.97 mg/l for A, B and C, respectively.

correlation between the initial Cd concentration and the equilibrium pH. It is, however, not feasible to explain the decrease in pH observed in Figure 4.2 in terms of the above theories.

The reason for this behaviour may lie in the fact that the experiment was not carried out under nitrogen gas, thus exposing the compost to oxygen. This exposure to oxygen, particularly at high pH, could result in chemically or bacterially mediated oxidation of the compost, which would generate more acidic groups and lower the pH. Furthermore, at high pH, base catalyzed hydrolysis of esters and peptides, releasing additional carboxylic acids, might occur, contributing to the decrease in pH. Since the decrease in pH only occurred above pH values of approximately 6 to 7.5, and no correlation between the initial Cd concentration and the equilibrium pH is evident from Figure 4.3, the decrease in pH may have been due predominantly to oxidation and hydrolysis reactions. Note that since the reaction vessels (centrifuge tubes) were sealed, the effect of CO₂ dissolution on pH can be regarded as negligible. The extent of the above-mentioned acid-forming reactions could be such that the effect which Cd addition might have on pH is masked.

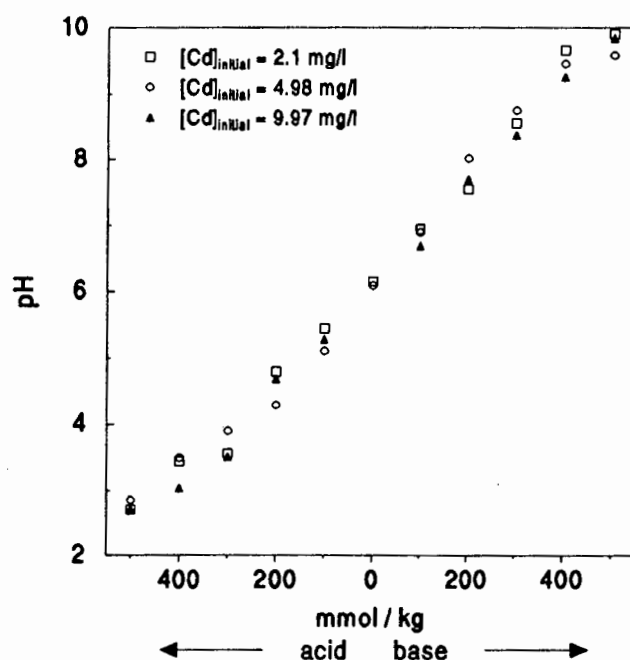


Figure 4.3 : pH of composted sewage sludge suspensions after equilibrating with cadmium at different initial concentrations.

4.4.2 Batch isotherm studies

The detailed results of the adsorption isotherm experiments are presented in Appendix 5 on the basis of which the adsorption isotherms shown in Figure 4.4 were constructed. Before discussing the adsorption isotherms, it should be pointed out that the electrical conductivity readings showed a high degree of uniformity within experiments, except in the case where

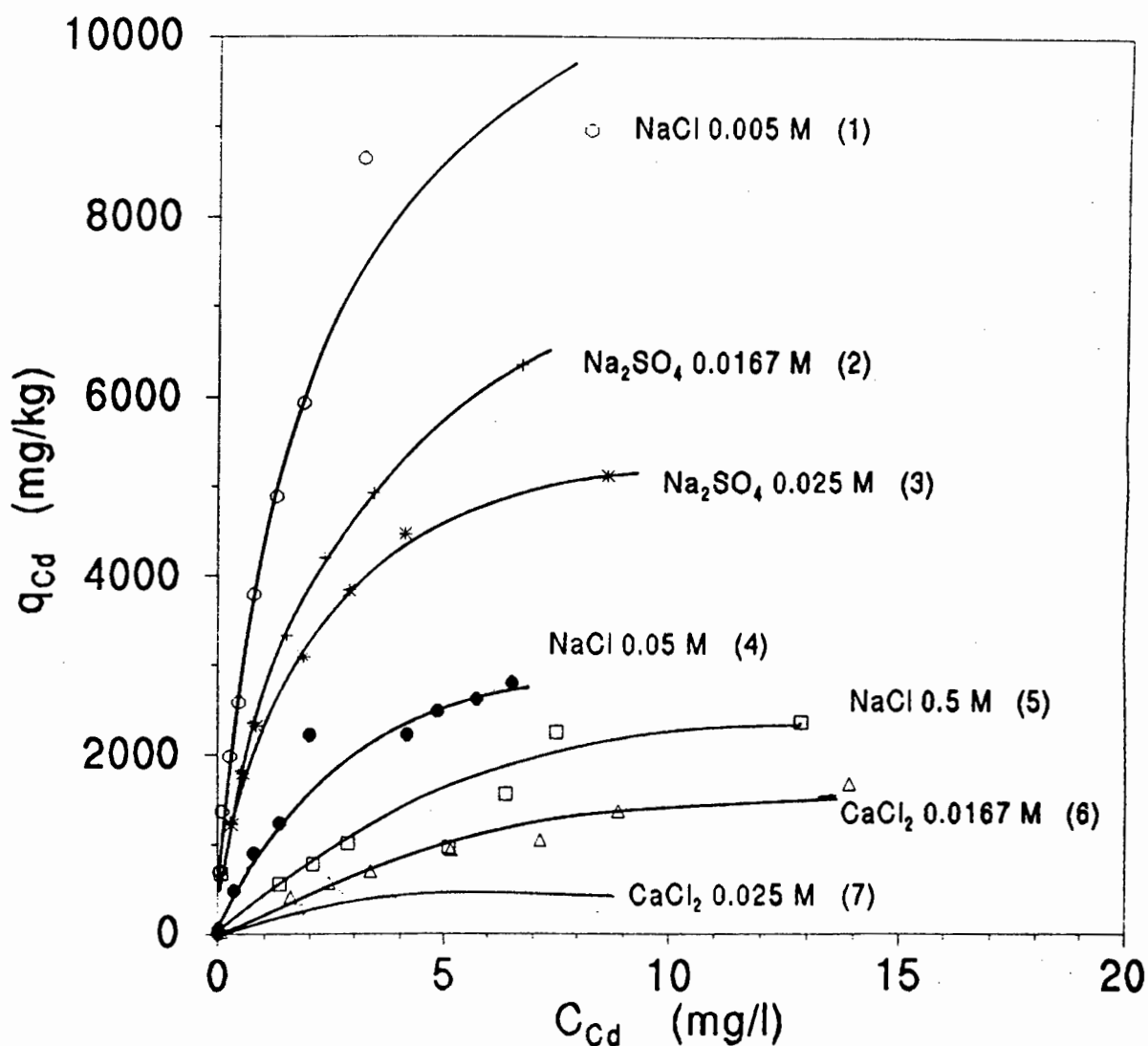


Figure 4.4 : Adsorption isotherms of the concentration of adsorbed Cd (q_{Cd}) plotted against equilibrium Cd concentration (c_{Cd}) with three background electrolytes at varying concentrations (curves drawn by hand)

0.005 M NaCl was used as the background electrolyte. In the latter case, a steady increase in EC was observed with increasing initial Cd concentration brought about by the addition of $CdSO_4$ solution. It will be shown later in this discussion that the SO_4^{2-} anion has a much smaller effect on Cd adsorption than the Cl^- anion. Since there were roughly seventeen times the charge equivalents of chloride ion relative to sulphate ion, it can be concluded that the effect of the sulphate anion on Cd adsorption was negligible, and the experiment in which the concentration effect of a single background electrolyte on Cd adsorption was investigated using solutions of 0.005, 0.05, and 0.5 M NaCl can therefore be regarded as having been a valid test for the effect of background electrolyte concentration. It should

also be pointed out that pH values within and between the experiments remained fairly uniform, and fell mostly within the range of pH 6.8 to 7.2. Since pH has a very small effect on Cd adsorption in this range (Figure 4.1), the pH pertaining to the adsorption isotherm experiments can be considered to have been effectively constant.

Based on the adsorption isotherms plotted in Figure 4.4, a number of different effects can be identified and these will be discussed in the ensuing sections.

4.4.2.1 Effect of electrolyte concentration on Cd adsorption

Increases in background electrolyte concentration resulted in the suppression of the adsorption isotherms (Figure 4.4). The adsorption capacity, as well as the initial slope of the adsorption isotherm, decreased with increasing background electrolyte concentration. There could be several reasons for this behaviour :

- a) The concentration of Cd^{2+} in solution decreases with increasing background electrolyte concentration. The anion of the background electrolyte may form strong bonds and stable species with Cd. For example, the well known species of Cd include CdSO_4 , $\text{Cd}(\text{SO}_4)_2^{2-}$, CdCl^+ , CdCl_2 , CdCl_3^- and CdCl_4^{2-} . The cationic species (CdCl^+) can still be adsorbed onto the compost, but less strongly than Cd^{2+} . Neutral, and negatively charged species are negligibly (or negatively) adsorbed by the surface.
- b) The cations of the background electrolyte compete with Cd for adsorption sites on the compost.

The degree to which each of these effects may have prevailed was investigated by assessing the effect of not only ionic strength but also the concentration and nature of the background electrolyte on Cd adsorption.

4.4.2.2 Influence of Cd^{2+} concentration on Cd adsorption

The assumption that the activity of Cd ions (calculated by the Debye-Huckel equation) in solutions of equal ionic strength, but containing different background electrolytes is false because of the speciation of Cd with the inorganic ligand species in solution. MINTEQA2 speciation predicts significant Cd speciation in the experimental solutions (Table 4.3).

From these predictions it is evident that the investigation of the effect of Cd activity on its adsorption becomes very complicated, since actual activity coefficients cannot be calculated

from the Debye-Huckel equation (for $I < 0.1$ M). This equation fails to account for specific ion pairing and complexation in solution (the extent of which differs, depending on the nature of the background electrolyte and its concentration) which may contribute more to the inequality between concentration and activity than the nonspecific electrostatic interactions modeled by the equation (McBride, 1994). This limitation is also true of other empirical expressions which convert measured concentrations to activities.

Table 4.3 : Calculated (MINTEQA2) speciation (%) of Cd in solutions with different background electrolytes at various concentration (Section 4.3.2).

Electrolyte (M)	Cd species (%)					
	Cd^{2+}	CdCl^+	CdCl_2	CdCl_3^-	$\text{Cd}(\text{SO}_4)_2^{2-}$	CdSO_4
NaCl (0.005)	74	25.8				
NaCl (0.05)	29	61.9	8.5			
NaCl (0.5)	3.6	42.6	39.6	14		
Na_2SO_4 (0.025)	3				11.5	45.3
CaCl_2 (0.025)	32	60	7.7			
Na_2SO_4 (0.0167)	48				7.6	44.1
CaCl_2 (0.0167)	39	55.6	5.1			

The higher the concentration of the complexing species, the higher the degree of complexation or ion-pairing. This statement is well illustrated by the MINTEQA2 calculations which predict increasing proportions of Cd complexed with chloride or sulphate ions as their concentration in solution increases (Table 4.3). The association constant for the reaction between Cd^{2+} and a particular ligand depends on the nature of the ligand, and the activity of the free Cd^{2+} ion will be small when high concentrations of ligands which have high affinities for Cd^{2+} are present.

Other major species (eg. Ca, Mg, PO_4) which are assumed to be present in the compost in concentrations similar to those given in Table 3.1, may have been dissolved from the

compost into the experimental solutions, but their effects on Cd adsorption were not taken into account in the modelling, since their exact concentrations in solution were not determined. However, even if all the Mg, Ca, and P (as ortho-phosphate) occurred in ionic form in solution, their concentrations would still be insufficient to influence Cd adsorption competitively (Mg, Ca), or inhibitably by speciating with Cd. This is because the concentrations of the background electrolytes in the experiments were high relative to those of other metals or ligands in the compost. It was therefore assumed that the omission of these components from the MINTEQA2 calculations would have no significant effect on the predicted Cd speciation.

From these data (Table 4.3) it is evident that in those solutions with background electrolyte ionic strength of 0.05 M (i.e. 0.05 M NaCl and 0.0167 M Na₂SO₄ or CaCl₂), Cd²⁺ concentrations are unequal. This was a result of the different extents of Cd interaction with anionic ligands in solution which depended on the nature of the electrolyte.

4.4.2.3 Background electrolyte anion effects

Curves 3 and 4 (Figure 4.4) are derived from experiments in which the Na⁺ concentration, as well as the charge equivalents of SO₄²⁻ and Cl⁻ were equal. These plots, however, are considerably different from one another. Although they have the same shape, the adsorption capacity, and initial slope, observed in plot 4 (and also calculated mathematically in Section 4.4.2.5) are lower than that of plot 3. These differences are very likely attributable to the nature of the predominant anions in the background electrolytes. Cadmium (II) speciates to a large extent with Cl⁻ ions, forming the species CdCl⁺, CdCl₂(aq), CdCl₃⁻ and CdCl₄²⁻, as well as with SO₄²⁻ ions, forming the species CdSO₄ and Cd(SO₄)₂²⁻. Neutrally- and negatively-charged species would not be adsorbed by the compost since the compost is predominantly a cation exchanger having only negatively charged adsorption sites in the pH range studied, and an overall negative surface charge. The differences in these adsorption isotherms is caused by the nature of the speciation, as well as the extent to which the speciation occurs with different electrolytes.

From Table 4.3 it is apparent that although a higher proportion (90%) of Cd is in a form which can be adsorbed by the compost when the background anion is chloride (i.e. in cationic form), the actual amount adsorbed is lower than when the background anion is sulphate, even though only 43 % of the Cd in the sulphate system is available for

adsorption. The CdCl^+ species is much less strongly adsorbed to the compost than the Cd^{2+} species since it is larger and monovalent, and thus has a much lower ionic potential (charge : radius ratio). The amount of Cd adsorbed seems to be correlated more with the percentage of Cd in the Cd^{2+} state than the amount of adsorbable Cd. In the experiments where sodium based electrolytes were used, a strong correlation was found between the adsorption capacity and the predicted percentage of the Cd^{2+} . A plot of complexation capacity ($q_{\text{Cd}}(\text{max})$) calculated for all seven adsorption isotherms (Section 4.4.2.5) against predicted Cd^{2+} percentage is shown in Figure 4.5. A regression analysis of the data points which originated from experiments in which sodium was used as the background electrolyte showed a good fit with a correlation coefficient (r^2) of 89 %.

This trend has been found by Naidu *et al.* (1994) who investigated the effect of Cl^- , SO_4^{2-} , and NO_3^- on adsorption of Cd by soils, and observed that chloride and nitrate had a far greater inhibiting effect than sulphate on Cd adsorption.

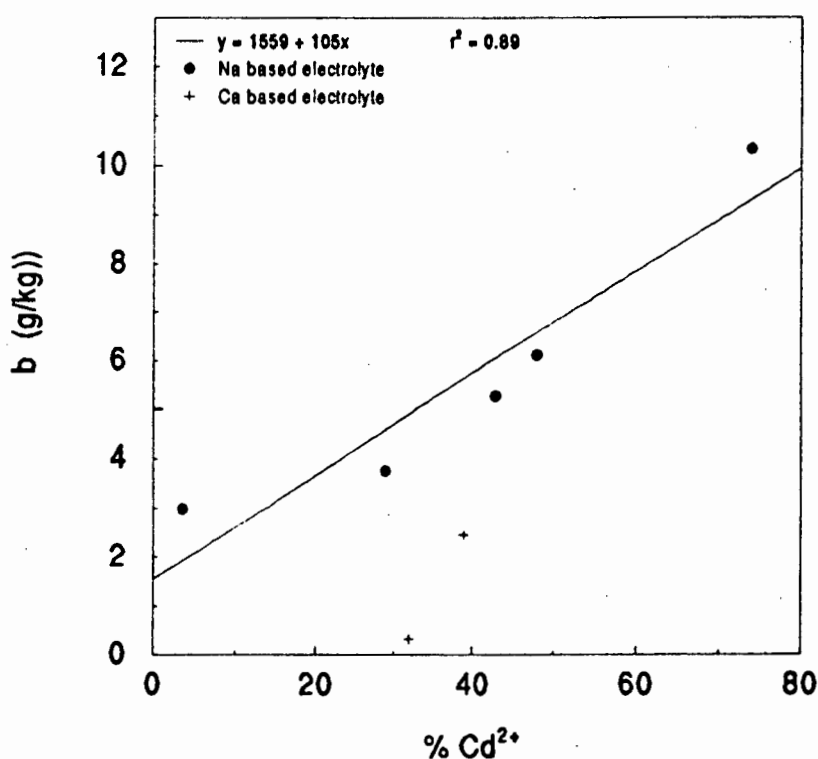


Figure 4.5 : Complexation capacity measurements (b values) calculated from the Langmuir isotherm and plotted as a function of predicted Cd^{2+} percentage in solution.

4.4.2.4 Background electrolyte cation effects

The effect of the nature of the cationic species in solution on Cd adsorption can also be deduced from the experimental results. Plots 7 and 4 (Figure 4.4) were obtained from experiments in which the nature and concentration of the background anion (Cl^-) were identical. The nature of the *cations* in each of the experiments, however, was different (Ca^{2+} and Na^+ , for plots 7 and 4, respectively) although they were present in equivalent concentrations (based on valence). The speciation distribution of Cd in the Cd-chloride complexes (Table 4.3) was almost identical in each case. However, the adsorption isotherms obtained under each of these experimental conditions were very different, and can probably be explained by Ca^{2+} ion competition with Cd for adsorption sites on the compost being stronger than that of Na^+ , resulting in relatively lower levels of Cd adsorption when Ca^{2+} is used as the background electrolyte. Non-specific adsorption of Cd is primarily affected, since competition is predominantly for the weaker, outer-sphere bonds where adsorption involves electrostatic interactions. Indeed, most experiments that attempt to measure *specific* adsorption employ a background electrolyte such as 0.01 M CaCl_2 , thereby inhibiting non-specific exchange of trace metal cations by competition (McBride, 1994).

A comparison of plots 2 and 6 (Figure 4.4), for which equivalent concentrations (based on valence) of Na_2SO_4 and CaCl_2 , respectively, were used as background electrolyte, shows the combined effects of Ca^{2+} competition and Cd-chloro speciation on adsorption, relative to Na^+ competition and Cd-sulphate speciation. In a study by Raspor *et al.* (1977) of Cd (II) complexation by nitrilotriacetate (NTA) in the presence of Na^+ , Ca^{2+} , Mg^{2+} and Cl^- , it was found that Cl^- competed markedly with NTA for Cd^{2+} . Ca^{2+} and Mg^{2+} were found to exert a much greater influence than Cl^- by competing with Cd^{2+} for NTA, which complexes these metals through carboxylic functional groups. It is therefore not surprising that the same trends were observed in the current adsorption experiments.

4.4.2.5 Conditional stability constants and complexation capacities

Using the equations described in Section 4.2.4, plots of $[\text{M}_\text{F}]/[\text{M}_\text{B}]$ against $[\text{M}_\text{F}]$ were made (Figure 4.6), and stability constants and complexation capacities were determined from the intercept and slope, respectively. The data used for plotting these graphs are given in Appendix 5. Two sets of data points were apparent within each of the experiments, and by fitting two best-fit straight lines to the data points (Figure 4.6), stability constants and complexation capacities for each set were determined. The high correlation coefficients of

these best fit lines indicate that it is reasonable to assume that there are two different distributions of the data.

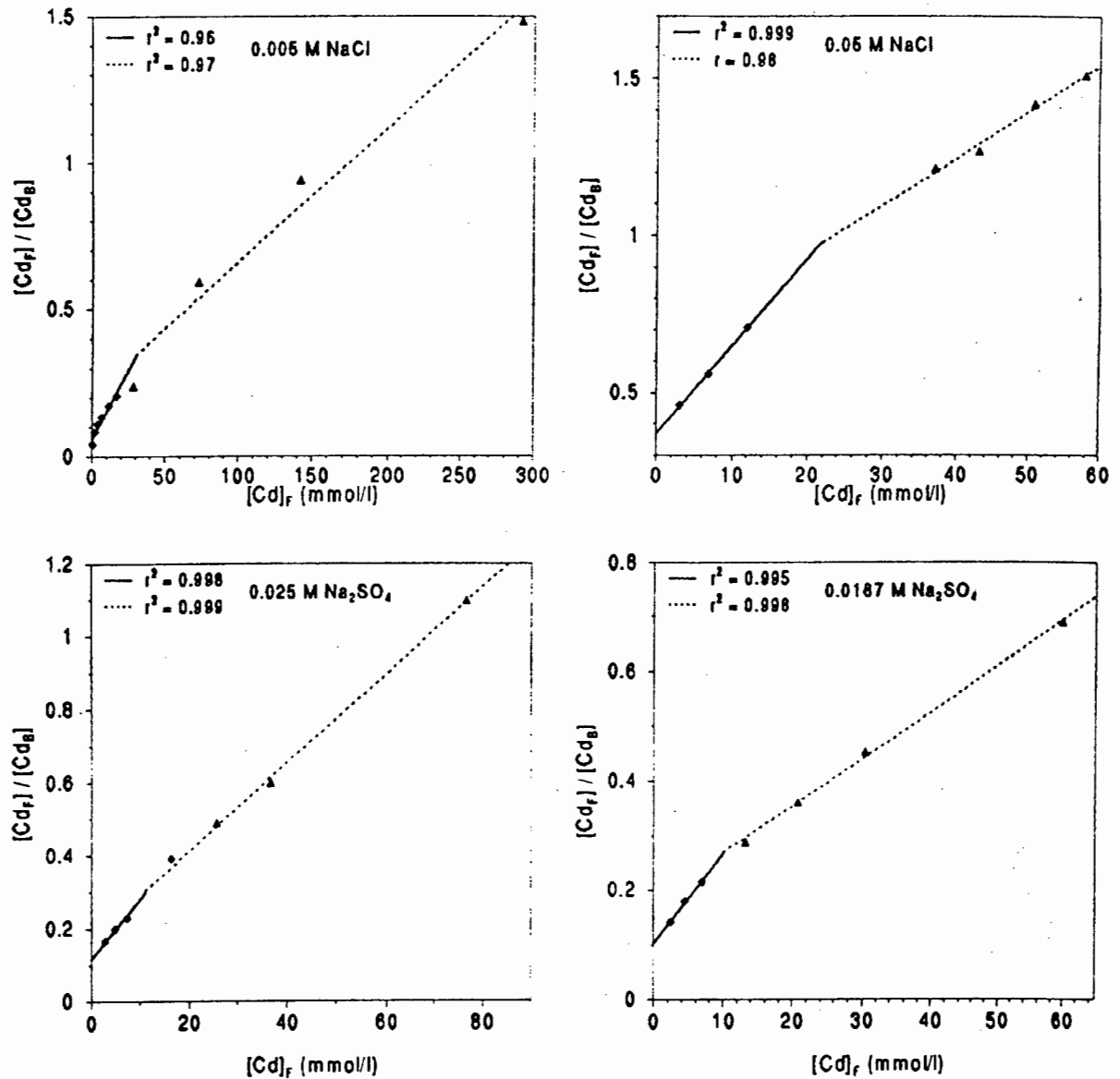


Figure 4.6 : Plots of $[Cd_F]/[Cd_M]$ against $[Cd_F]$ for adsorption experiments run in the presence of different background electrolytes at various concentrations (Appendix 5, Table A5.9 for equations of regression curves)

Two different types of ligands are assumed to be in operation in this system, causing the segregation of the two sets of data: those with high Cd-ligand conditional stability constants (K_A) but present in low concentrations ($[L_A]$), and those with lower Cd-ligand stability constants (K_B) but present in higher concentrations ($[L_B]$). At low equilibrium Cd concentrations, the steeper slope and lower intercept of the fitted curves imply that there are low concentrations of Cd binding sites which have high conditional stability constants

for Cd binding. Conversely, there are higher concentrations of less selective binding sites in the compost which only become occupied once the stronger adsorption sites are saturated. These data are presented in Table 4.4. and are further discussed in Section 4.4.2.6. The concentration of Cd complexing ligands, $[L_A]$ and $[L_B]$, can be equated to the amount of Cd which can be adsorbed allowing indirect measurement of the complexation capacity.

Another method, exploiting the Langmuir equation, was also used to measure complexation capacities from the b value in the linear equation which is obtainable from the intercept of the plot of $1/c_{Cd}$ against $1/q_{Cd}$. These data are presented in Table A5.8 in Appendix 5 and are plotted in Figure 4.7. The Langmuir b values are listed in Table 4.4. As can be seen from these plots and the regression coefficients of best-fit straight lines through the data points, the data fit the Langmuir isotherm very closely.

It is important to note that the conditional stability constants and the complexation capacities measured by the above methods are subject to the experimental conditions of pH, ionic strength, nature of inorganic species in solution and the relative concentrations of the Cd-compost and Cd-inorganic species. Direct comparisons of these data with those obtained by other studies are therefore only possible if similar or equivalent conditions were used in their determination.

From Table 4.4 it can be seen that a certain degree of correlation exists between the b values obtained from the Langmuir equation and $[L_A]$ and $[L_B]$. The b value consistently lies between $[L_A]$ and $[L_B]$. Conditional stability constants for the stronger complexes (K_A) are observed to increase with decreasing concentration of the same background electrolyte. This trend is almost reversed for the weaker complexes (K_B). There is a much greater distinction between conditional stability constant values of the two types of complex formed (i.e. between K_A and K_B), the K_A values being significantly higher, indicating a higher strength of adsorption. The concentration of strong bonding ligands ($[L_A]$) is almost half that of the weaker bonding ligands ($[L_B]$). Another distinction can be made between the conditional stability constants (K_A or K_B) obtained from the experiments where 0.05 M NaCl and 0.025 M Na_2SO_4 were used as background electrolytes. Although there were equivalent concentrations (based on valence) of cations and anions in each of these experiments, the conditional stability constants were considerably higher when the background electrolyte was Na_2SO_4 , providing a quantitative expression for the higher complexation capacity of the

compost under these conditions relative to when NaCl was used as background electrolyte.

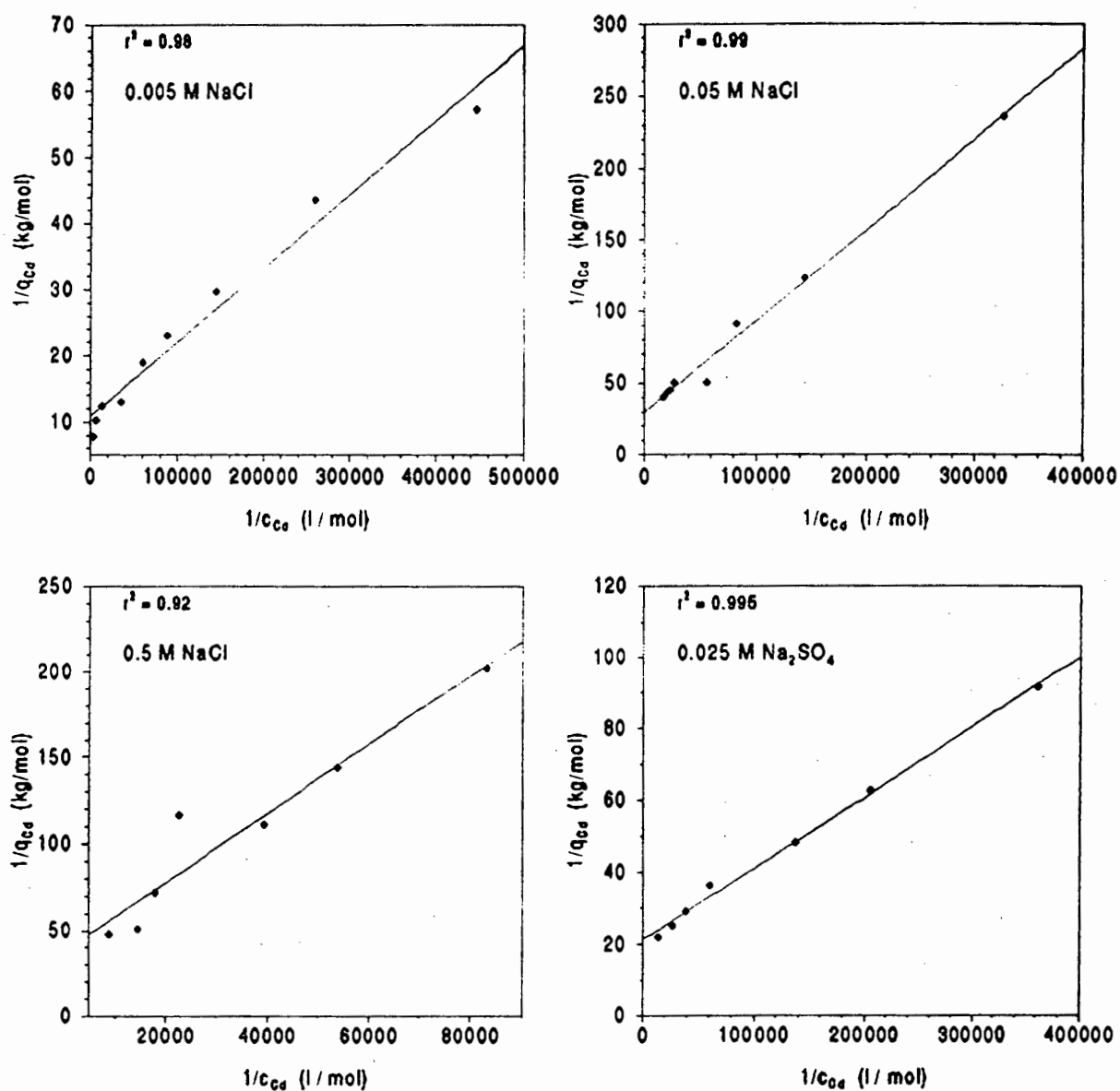


Figure 4.7 : Langmuir isotherm plots from adsorption experiments run in the presence of different background electrolytes at various concentrations (see Appendix 5 for equations describing regression curves)

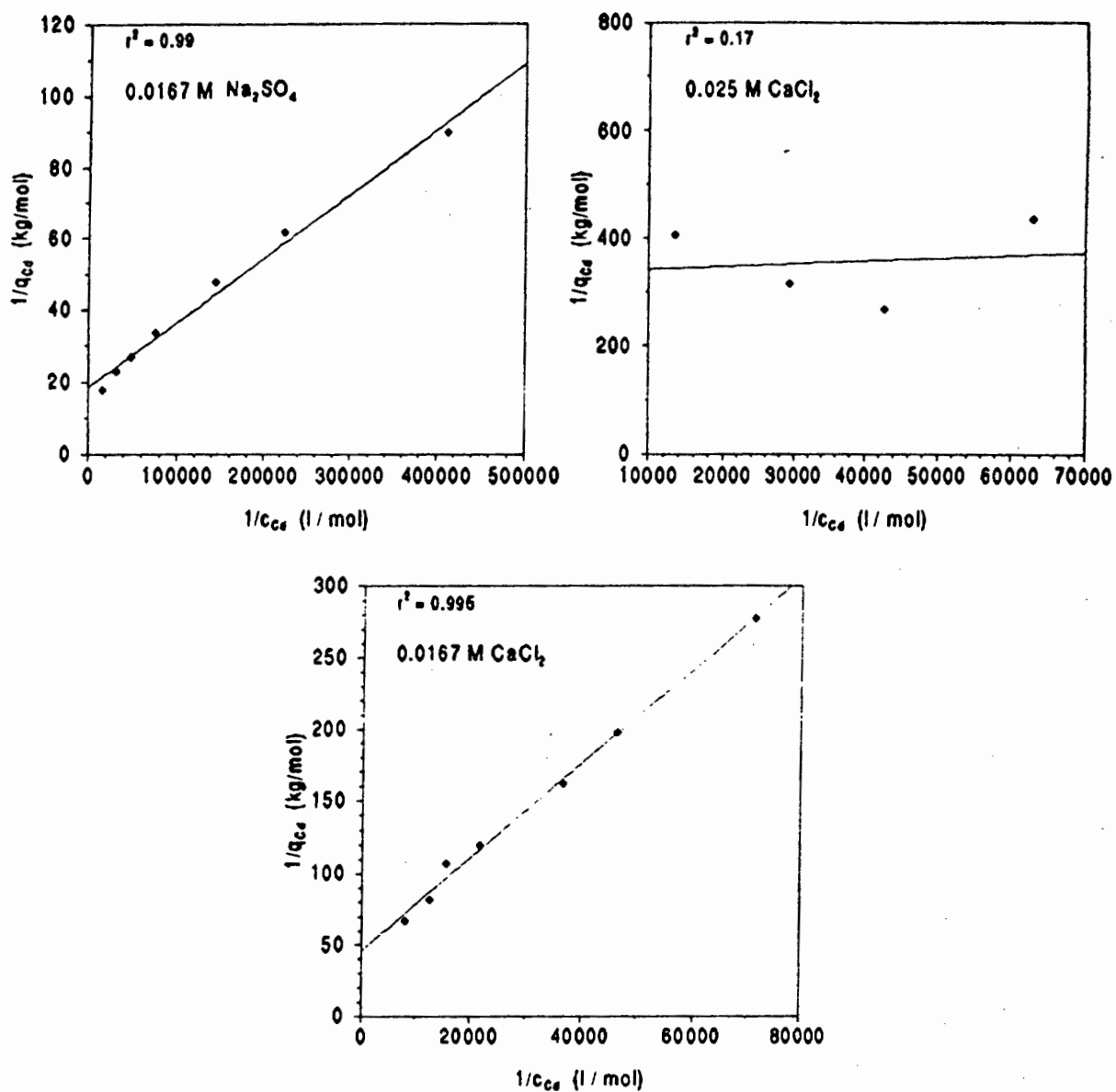


Figure 4.7 (continued)

Table 4.4 : A comparison of the results of two methods of determining complexation capacities of compost for Cd, as well as the conditional stability constants associated with the complexation.

Electrolyte	Langmuir b (mg Cd/kg)	$[L_A]^*$ (mg Cd/kg)	$[L_B]^*$ (mg Cd/kg)	$\log K_A^{**}$	$\log K_B^{**}$
NaCl 0.005 M	10 340	7 576	15 905	5.22	4.34
NaCl 0.05 M	3 764	2 601	4 836	4.87	4.36
NaCl 0.5 M	2 986				
Na ₂ SO ₄ 0.025 M	5 265	4 340	5 955	5.16	4.85
Na ₂ SO ₄ 0.0167 M	6 129	4 420	8 467	5.20	4.67
CaCl ₂ 0.0167 M	2 462				

* $[L_A]$ and $[L_B]$ refer to concentrations of strong- and weak-bonding sites respectively.

** K_A and K_B refer to the conditional stability constants of strong- and weak-bonding sites, respectively.

Viraraghaven and Dronamraju (1993) found that horticultural peat originating in Saskatchewan, Canada, was effective in adsorbing Cu, Ni and Zn from wastewater. Complexation capacities in their experiments for Cu, Ni and Zn were approximately 6, 4 and 4 g/kg peat, respectively. The percentage removal of these metals from solutions containing initial concentrations of 1 mg/l ranged between 50 and 60 %. Although the complexation capacity of the peat with respect to Cd was not studied, the affinity of cation exchange materials for Cd is generally lower than that for Ni, Zn and Cu (Section 1.7.2). Therefore, since the complexation capacity of the peat studied by Viraraghaven and Dronamraju (1993) for Ni, Zn and Cu was within the same approximate range as that of composted sewage sludge for Cd (on a molar scale) obtained in the present study (Table 4.4), it is reasonable to assume that composted sewage sludge has approximately the same, if not higher, complexation capacity for heavy metals as the horticultural peat. Complexation capacities of peat originating from Albertamy (West Bohemia) for Zn, Cu and Pb, studied by Horacek *et al.* (1994) are approximately 120, 60 and 160 g/kg, respectively. These values are much higher than those found for Cd in the present study (on a molar basis)(Table 4.4). Possible reasons for this may be that the peat used in the study by Horacek *et al.* (1994) was

pretreated by loading with calcium prior to the adsorption studies; the affinity of cation exchange materials is typically higher for Zn, Cu and Pb than for Cd (Section 1.7.2); and the peat used in the study by Horacek *et al.* (1994) may have been humified to a greater extent and in a greater state of subdivision with a larger specific surface.

Non-humified biomass materials which have been studied with respect to their potential as biosorbents include *Ascophyllum nodosum*, a common marine brown alga. Studies have shown that this alga can accumulate between 30 and 100 g Cd/kg algae (Holan *et al.*, 1993; Volesky and Prasetyo, 1994). The alga thus seems to outperform the composted sewage sludge as a biosorbent. However, it should be noted that the pretreatment of the algae before the adsorption studies was extensive. The algae are first ground to approximately 70 μm , then immobilised in a column by crosslinking the particles. Furthermore, the adsorption studies performed on the algal biomass were at zero ionic strength which would result in enhanced complexation capacities relative to those which would have been obtained if ionic strengths similar to those in the present study were used. Algal biomass adsorption of Cd does, in addition to its high Cd complexation capacity, have other advantages : the pH at which adsorption experiments on the algae were carried out (Volesky and Prasetyo, 1994; Holan *et al.*, 1993) were at lower pH (4 to 6) than the present study, and Cd desorption with acid from the algae resulted in no changes in adsorption capacities.

4.4.2.6 Efficiency of Cd removal from solution as a function of concentration

The efficiency of Cd removal from solution where 0.0167 M Na_2SO_4 was used as a background electrolyte was calculated at each of the initial Cd concentrations. The results are presented in Table A6.1 (Appendix 6) and plotted in Figure 4.8. The decrease in adsorption efficiency with increasing initial Cd concentration was expected because the strong complexing ligands which are present in low concentrations become saturated first (Gardiner, 1975). In a study of metal complexation by sewage sludge (Lake *et al.*, 1989) it was found that two types of complex were formed by each metal (including Cd), the first being in much lower concentration but having higher stability constants than the second. Viraraghavan and Dronamraju (1993), in a study on the adsorption characteristics of Cu, Ni, and Zn by peat, found that the absolute amount of metal adsorbed increased, whilst the percentage adsorbed decreased with increasing initial concentration of metal in solution. These studies indicate that at low metal ion concentrations complexation is controlled mainly by stronger bonding sites, whereas at higher metal ion concentrations the stronger

sites become fully occupied and weaker sites start to become involved in complexation. Evidence for this behaviour was indeed found in the present study and has been discussed in Section 4.4.2.5, where higher concentrations were found of weak-bonding sites ($[L_B]$) with lower stability constants (K_B), relative to the lower concentrations of strong-bonding sites ($[L_A]$) with significantly higher stability constants (K_A).

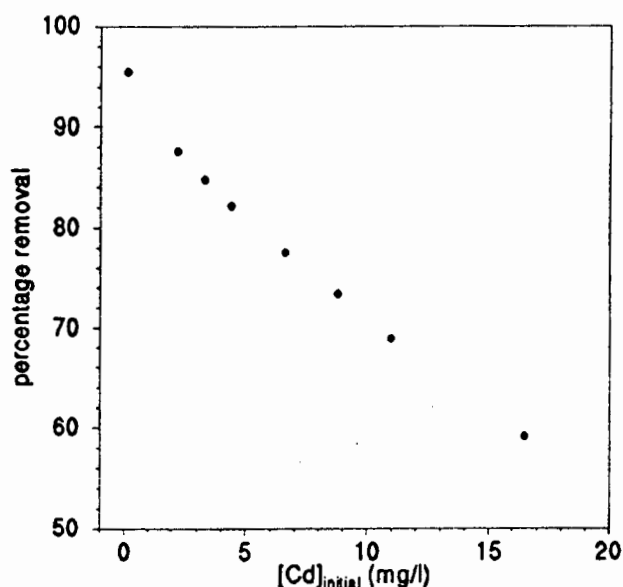


Figure 4.8 : The percentage of Cd removed by composted sewage sludge plotted as a function of initial concentration of cadmium in the presence of 0.0167 M Na_2SO_4 as a background electrolyte.

4.4.2.7 Desorption experiments

Table 4.5 lists the amount of Cd adsorbed in each of four suspensions using different background electrolytes, the amount of Cd desorbed using two different acids, and the extent of Cd adsorption following the desorption treatment.

The efficiency of desorption did not vary significantly with the type of acid used, but was affected by the amount of Cd initially adsorbed on the compost. Those samples of compost to which large amounts of Cd were adsorbed (those where $[Cd]_{initial}$ was 16.5 mg/l) showed a high efficiency of extraction relative to those in which smaller amounts of Cd were adsorbed. Once again, the reasoning for this behaviour centres around the strength of adsorption. In previous experiments in this study, the compost was shown to adsorb Cd more strongly at lower Cd concentrations than at high Cd concentrations. Hence the Cd

which is less strongly bound, is more easily desorbed, leading to the higher observed desorption efficiency in the more Cd-enriched systems.

After the acid treatment, the Cd adsorption efficiency of the compost decreased markedly. Holan *et al.* (1993) and Volesky and Prasetyo (1994) found, in desorption studies of Cd from the marine brown algae *Ascophyllum nodosum*, *Fucus vesiculosus* and *Sargassum natans* which had been loaded with Cd, that desorption of Cd using 0.1 to 0.5 M HCl resulted in no changes in the Cd uptake capacity through five successive adsorption/desorption cycles.

Table 4.5 : Experimental data from Cd desorption experiments involving composted sewage sludge, showing initial adsorption, percentage desorption after the first acid induced desorption step, and the relative ability of the compost to adsorb Cd after the desorption treatment.

[Cd] _{initial} (mg/l)	Acid used for desorption (0.1 M)	q _{Cd} (mg/kg)	Desorption efficiency after first desorption step (%)	q _{Cd} after desorption treatment	
				(mg/kg)	Relative % (to initial q _{Cd})
16.5	H ₂ SO ₄	6487	95	5263	81
16.5	HCl	6942	94	5585	80
11	H ₂ SO ₄	4550	84	3333	73
11	HCl	4673	79	3600	77

4.4.3 Column experiments

4.4.3.1 Reproducibility tests

The pH of effluent collected after passing known volumes of 0.01 M NaOH solution through compost columns is plotted in Figure 4.9 and the associated experimental data are presented in Appendix 7. The breakthrough curves shown in Figure 4.9 are well superimposed upon one another and from a visual assessment, one can say that the method has a high degree of reproducibility.

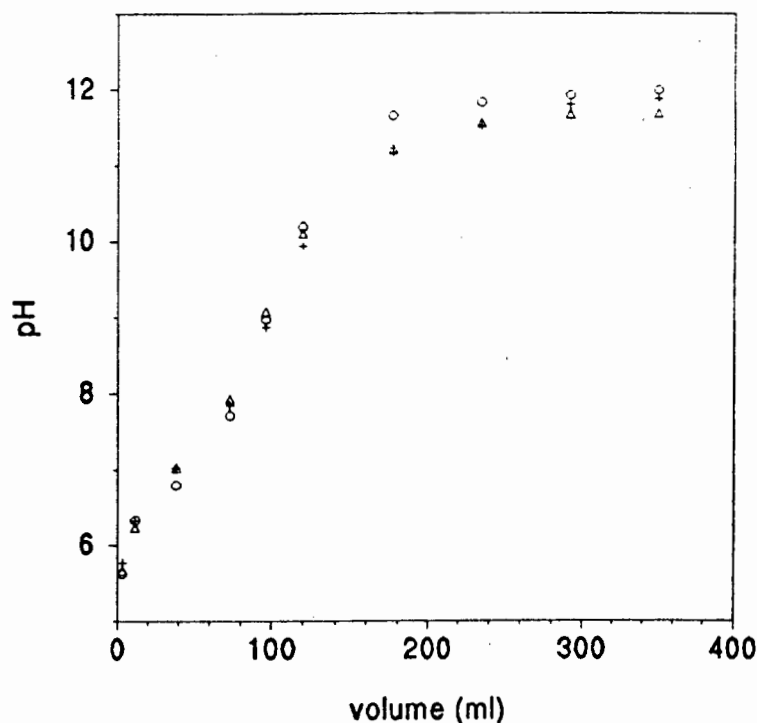


Figure 4.9 : Graph of pH against volume of 0.01 M NaOH passed through the column, for three replications.

4.4.3.2 Cadmium breakthrough curves

The Cd concentrations in the eluent samples collected at specified time intervals, and the volume of Cd solution passed through the column are reported in Appendix 8 (Table A8.1) and are plotted in the breakthrough curve shown in Figure 4.10. A full breakthrough curve was not obtained and any deductions from this experiment are limited since the various factors having an influence on Cd adsorption in the column, such as flow rate, Cd concentration and ionic strength, were not explored due to time constraints. However, some of the information obtained from this experiment is quite useful in that it shows the approximate amount of Cd which can be extracted from a solution containing 5.54 mg/l of Cd and 0.05 M NaCl, flowing at a rate of 80 ml/hr through 6 g of compost retained in a 16 mm diameter column.

Breakthrough occurred after approximately 1800 ml of Cd solution had passed through the column. This translates to a flow rate of 13.3 l/(hr.kg) being maintained for 23 hours before breakthrough takes place. The Cd loading on the compost at the point of breakthrough was 1660 mg/kg. This may seem to be a small volume of effluent and a low loading of the

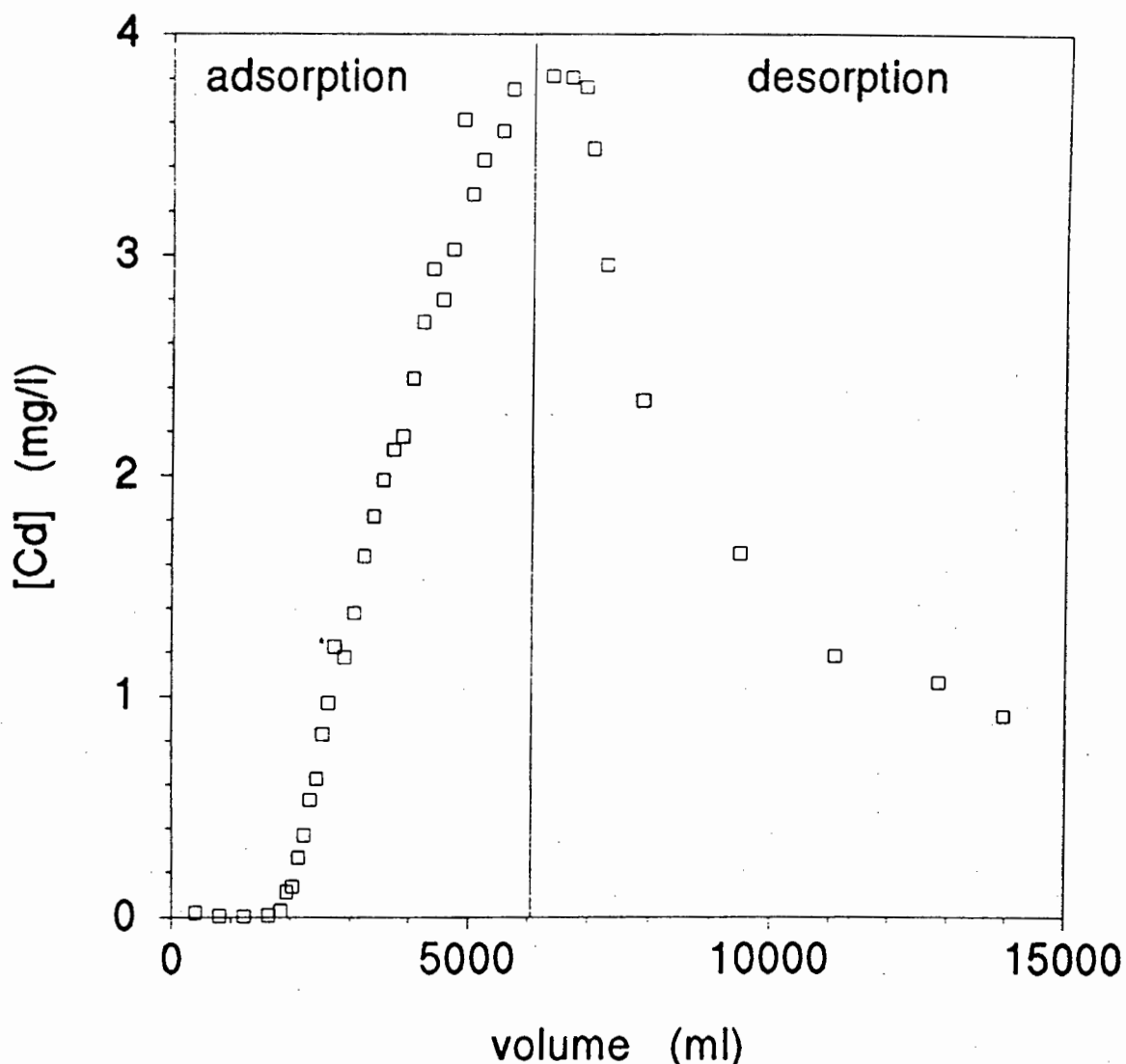


Figure 4.10 : Breakthrough curve prepared by passing 5.54 mg/l Cd solution through a 6g sample of compost. Desorption was effected by replacing the Cd solution with 0.05 M NaCl solution after 6000 ml of eluent had passed through the column.

compost, but since effluents may typically contain Cd at lower concentrations and ionic strengths, the breakthrough time/volume for Cd-bearing effluents would be expected to be much higher, particularly if the chloride concentration in solution is lower. In addition, typical wastewater ion exchange treatment processes involve passing effluent consecutively through several columns arranged in series, so that the last column in the series is the least contaminated. As the ion exchange material in the final column approaches breakthrough, it is shifted to the second-last column and fresh ion exchange material is used in the final column. In this way, loading of the compost, were it to be used for this purpose, could far exceed that at which breakthrough occurs, thus optimizing its use as a biosorbent.

4.4.3.3 *Column desorption*

Data pertaining to Cd concentrations in the column effluent after the Cd solution had been replaced by a 0.05 M NaCl solution is given in Appendix 8 (Table A8.2) and is plotted together with the breakthrough curve in Figure 4.10.

Desorption of Cd from the column was initially very fast. As more 0.05 M NaCl solution passed through the column, however, the rate of Cd desorption decreased, probably in response to a combination of two factors. Initially, the difference in Cd concentration between the compost and the solution was high, resulting in rapid desorption of Cd. As more Cd desorbed, the difference in concentrations decreased, leading to a slower rate of desorption. In addition, Cd complexation is stronger at low levels of adsorption, resulting in a reduced rate of desorption as increasing volumes of 0.05 M NaCl are passed through the column. This has been extensively discussed in Sections 4.4.2.5 and 4.4.2.6.

4.5 Conclusions

The composted sewage sludge has a high complexation capacity for Cd, up to approximately 10 g/kg dry mass at low ionic strength, and can be used to effectively remove Cd from solutions of low Cd concentration. Since the affinity of cation exchange materials for heavy metals is generally of the order $\text{Cd} < \text{Ni} < \text{Zn} < (\text{Pb}, \text{Cu})$, it is likely that composted sewage sludge may be used to effectively remove Ni, Zn, Pb and Cu from heavy metal-contaminated solutions.

Cadmium adsorption is enhanced with increasing pH between pH 3 and 7.5. Below pH 3, there is no significant adsorption of Cd by the compost and at pH 7.5 maximum adsorption of Cd occurs with no further increase at higher pH values. This phenomenon is probably related to the increasing dissociation of acidic functional groups with increasing pH, resulting in greater electrostatic attraction and capacity of the compost for cationic Cd species.

Composted sewage sludge in an aqueous suspension, exposed to air and at high pH, undergoes hydrolysis and oxidation reactions if allowed to stand for extended time periods. These reactions can cause a significant decrease in the pH of the suspension. The time required for these reactions to occur to a significant extent is not known from this study, but after 24 hours these reactions do cause significant changes in pH of suspensions.

Increasing the background electrolyte concentration of a single electrolyte results in decreased Cd adsorption, illustrated by suppression of adsorption isotherm plots with increasing electrolyte concentration. The nature of the background electrolyte can have a pronounced effect on Cd adsorption. Sulphate ions in solution cause a relatively small decrease in adsorption of Cd compared to chloride ions in solution. The differences observed are intimately related to the nature of the speciation between these anions and Cd in solution. A strong correlation exists between the concentration of Cd adsorbed and the percentage of Cd in the Cd^{2+} form for experiments where Na-based electrolytes are used. The effect of cations on Cd adsorption is due to competition of these for adsorption sites on the compost. Calcium ions compete much more vigorously for adsorption sites thus, causing greater decreases in Cd adsorption than do Na^+ ions.

There are two types of bonding sites for Cd on composted sewage sludge : those in low concentrations but with high conditional stability constant values (K_c), and those in higher concentrations but with low K_c values. Conditional stability constant values increase with decreasing ionic strength and are also affected by the nature of the background electrolyte. Chloride based electrolytes cause greater decreases in K_c values than do sulphate based electrolytes in experiments in which there are equal equivalents of these anions.

The absolute amount of Cd adsorbed by compost in aqueous suspension increases with initial Cd concentration, but the efficiency (percentage) of adsorption increases with decreasing initial Cd concentrations.

The acids HCl and H_2SO_4 show no significant differences in desorption efficiency of Cd from composted sewage sludge. Desorption using HCl and H_2SO_4 results in a decrease in complexing efficiency of the compost for Cd of approximately 20 to 30 % .

Breakthrough curves yielded a limited amount of information, and more work needs to be done on this aspect before yielding more information from which useful conclusions can be made.

4.6 Recommendations for possible further work

The pretreatment of composted sewage sludge, either by loading with a cation such as Ca^{2+} or K^{+} , or by converting it to the H^{+} form by acid treatment would make experimental data more amenable to comparison with data obtained from studies of other materials which are often pretreated before being used for experiments. For example, experimental data obtained for the determination of total acidity are purely empirical and depends on the degree of substitution of other cations on the compost.

The study of the adsorption characteristics of the compost with respect to other heavy metals which are abundant in a wide range of wastewaters, such as Ni, Cu, Zn, Fe and Cr would be necessary before using the compost as an adsorbent in wastewaters where these metals are present. The interaction and competing effects of these metals with one another should also be studied by means of adsorption experiments in which mixtures of metals in solution are equilibrated with composted sewage sludge suspensions. Furthermore, the mineralogy of the compost should be investigated so that its contribution to adsorption and other properties can be assessed.

Temperature has been shown to have a marked effect on heavy metal adsorption by some humified materials, and although the experiments in the present study were all performed at room temperature, it would be useful to determine the extent to which metal adsorption is affected by temperature. Furthermore, the time necessary for equilibration to occur between composted sewage sludge and the heavy metal of interest should be determined to ensure that the reactions have run to completion, also so that the equilibration time can be minimised to prevent oxidation reactions from significantly denaturing the compost and decreasing the pH of the suspensions. Another way of avoiding the oxidation reactions may be to conduct all experimental work under nitrogen gas.

The nature of the background electrolytes used in the experiments were shown to have significant effects on the adsorption of Cd from solution. Some of the most commonly occurring cations and anions were studied. There are, however, several other electrolytes which may be found in wastewaters and the effect of these on metal adsorption should be assessed.

Desorption using different desorbents which might have a smaller impact on metal removal in adsorption experiments following a desorption step should be considered. In particular,

from the data and interpretations discussed in the present study, CaCl_2 may prove to be an efficient reagent to effect the desorption of Cd from composted sewage sludge. Chloride speciation as well as competition for adsorption sites by Ca^{2+} ions might induce efficient desorption without decreasing the complexation capacity of the compost. Chloride speciation with most other heavy metals is not as significant as it is for Cd. Thus CaCl_2 may be less efficient in desorbing other metals compared to Cd.

The data obtained from column experiments is scarce and further experiments in which several parameters such as Cd concentration in solution, column proportions and flow rates are varied, would be necessary before useful interpretations and a realistic assessment of composted sewage sludge as an adsorbent for the treatment of heavy metal-contaminated wastewaters can be made.

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APPENDICES

Appendix 1

The Brunauer, Emmett, and Teller equation

The BET equation is :

$$\frac{P}{V(P_0 - P)} = \left(\frac{1}{V_m C}\right) + \left[\frac{(C - 1)P}{V_m C P_0}\right]$$

where V is the gas volume adsorbed at pressure P , V_m is the volume of gas required for a single molecular layer over the entire adsorbent surface, P_0 is the gas pressure required for saturation at the temperature of the experiment, and $C = \exp [E_1 - E_2]/RT$, where E_2 is the heat of liquification of the gas, E_1 is the heat of adsorption of the first layer of adsorbate, R is the gas constant, and T is the absolute temperature. The BET equation involves assumptions that (i) the heat of adsorption of all molecular layers after the first is equal to the heat of liquification and (ii) at equilibrium, the condensation rate on the surface is equal to the evaporation rate from the first or subsequent layers.

Appendix 2

CEC determination by the Gillman method

The cation exchange capacity of the size fractions < 2, 1-2, 0.1-1, and < 0.1, was determined using the Gillman method (Rhoades, 1992). Using this method, 2 g of air-dried compost, of each size fraction, and 20 ml of 0.1 M BaCl saturating solution was placed in preweighed centrifuge tubes. Duplicates of each size fraction were made (A and B). The centrifuge tubes were stoppered and placed on a reciprocal shaker for 2 hours. The solutions were then centrifuged, and the supernatant was decanted. The compost was then equilibrated with three successive 20 ml increments of 0.002 M BaCl₂ solution by shaking each for 1 hour between centrifugations, and discarding the supernatants. The centrifuge tubes plus compost were then weighed in order to determine the amount of 0.002 M BaCl₂ solution entrained following the last decantation of supernatant.

Additions of 10 ml of 0.02 M MgSO₄ to each of the centrifuge tubes containing size fractions < 2, 1-2, and 0.1-1 mm; and 10 ml of 0.05 M MgSO₄ to the size fraction < 0.1mm, were made. These were then sealed, and placed on a reciprocal shaker for 1 hour. The electrical conductivity of the reactant suspension was adjusted to that of a 0.0015 M MgSO₄ reference solution, by dilution with measured amounts of distilled water. The centrifuge tubes were then shaken overnight on a reciprocal shaker, followed by centrifugation. The supernatant was decanted, filtered through 0.45 μ m millipore filters, and retained for analysis. The pH of the solutions was also recorded using a Metrohm 691 pH meter, and Mg concentrations were determined by AAS (Section 3.3.3). The experiment was performed in duplicate.

Appendix 3

Experimental results of the potentiometric titration

Table A3.1 : Potentiometric titration data after overnight equilibration, and at $I = 0.1$ (experiment (i)).

	pH			
	Sample 1	Sample 2	Average	RSD (%)
NaOH added (mmol/kg)				
0	5.98	5.92	5.95	0.50
10	6.19	6.07	6.13	0.98
30	6.20	6.32	6.26	0.96
50	6.41	6.61	6.51	1.54
70	6.75	6.57	6.66	1.35
100	6.82	6.94	6.88	0.87
130	7.20	7.11	7.16	0.63
150	7.40	7.25	7.33	1.02
170	7.40	7.43	7.42	0.20
200	7.63	7.89	7.76	1.68
250	7.93	7.96	7.95	0.19
300	8.44	8.26	8.35	1.08
HCl added (mmol/kg)				
10	5.77	5.72	5.75	0.44
30	5.56	5.57	5.57	0.09
50	5.47	5.39	5.43	0.74
70	5.16	5.32	5.24	1.53
100	5.02	4.87	4.95	1.52
150	4.60	4.57	4.59	0.33
200	4.12	4.17	4.15	0.60
250	4.06	3.96	4.01	1.25
300	3.40	3.47	3.44	1.02

Table A3.2 : Potentiometric titration data after 30 minute equilibration and at $I = 0$, (experiment (ii)).

Moles of NaOH added (mmol/kg)	pH	Moles of HCl added (mmol/kg)	pH
0	5.92		
10	6.07	10	5.72
30	6.32	30	5.57
50	6.61	50	5.39
70	6.57	70	5.32
100	6.94	100	4.87
130	7.11	150	4.57
150	7.25	200	4.17
170	7.43	250	3.96
200	7.89	300	3.47
250	7.96		
300	8.26		

Appendix 4

Experimental data in the determination of the effect of pH on cadmium adsorption by the compost

Table A4.1 : Experimental data illustrating the effect of pH on Cd adsorption (initial [Cd] = 2.10 mg/l).

	pH_{init}	$pH_{equilib}$	$[Cd]_{equilib}$	q_i
Acid added				
(mmol/kg)				
500	2.70	2.75	2.12	0
400	3.44	3.50	1.97	0.78
300	3.56	3.63	1.85	15
200	4.79	4.94	0.92	70.8
100	5.44	5.67	0.52	94.8
0	6.15	6.35	0.23	112.2
Base added				
(mmol/kg)				
100	6.94	7.05	0.10	120.0
200	7.55	7.42	0.07	121.8
300	8.56	7.86	0.05	123.0
400	9.66	8.65	0.08	121.2
500	9.90	8.92	0.07	121.8

Table A4.2 : Experimental data showing the effect of pH on Cd adsorption (initial [Cd] = 4.98 mg/l).

	pH_{init}	$\text{pH}_{\text{equilib}}$	$[\text{Cd}]_{\text{equilib}}$ (mg/l)	q_i (mg/kg)
Acid added (mmol/kg)				
500	2.85	2.94	5.10	0
400	3.49	3.60	4.54	26.4
300	3.90	3.98	3.58	84
200	4.29	4.39	3.23	105
100	5.10	5.16	1.84	188.4
0	6.09	6.01	0.70	256.8
Base added (mmol/kg)				
100	6.89	6.71	0.39	275.4
200	8.01	7.38	0.18	288.0
300	8.75	7.84	0.14	290.0
400	9.46	8.78	0.15	289.8
500	9.58	8.91	0.16	289.2

Table A4.3 : Experimental data showing the effect of pH on Cd adsorption (initial [Cd] = 9.97 mg/l).

	pH _{init}	pH _{equilib}	[Cd] _{equilib} (mg/l)	q _i (mg/kg)
Acid added (mmol/kg)				
500	2.71	2.78	10.65	0
400	3.04	3.07	10.54	0
300	3.51	3.59	9.31	39.6
200	4.68	4.74	6.37	216.0
100	5.28	5.40	4.13	350.4
Base added (mmol/kg)				
100	6.68	6.83	0.96	540.6
200	7.70	7.48	0.45	571.2
300	8.37	7.84	0.29	580.8
400	9.26	8.36	0.26	582.6
500	9.84	9.76	0.30	580.2

Appendix 5

Results from adsorption isotherm studies

Table A5.1 : Adsorption experiment in which the background electrolyte was NaCl, at a concentration of 0.005 M.

$[\text{Cd}]_{\text{init.}}$ (mg/l)	$\text{pH}_{\text{equilb.}}$	$\text{EC}_{\text{equilb.}}$ ($\mu\text{S}/\text{cm}$)	C_{Cd} (mg/l)	q_{Cd} (mg/kg)	$[\text{Cd}_\text{f}]\times 10^3$ (mmol/l)	$[\text{Cd}_\text{f}]/[\text{Cd}_\text{b}]$
0.11	7.26	584	<.05	71		
2.20	7.23	594	0.09	1373	0.77	0.041
3.30	7.12	630	0.25	1980	2.24	0.083
4.40	6.97	639	0.43	2577	3.84	0.109
6.60	6.97	696	0.77	3785	6.88	0.133
8.80	6.90	646	1.28	4878	11.4	0.170
11.0	6.82	654	1.87	5926	16.6	0.205
16.5	6.75	731	3.18	8639	28.3	0.239
22.0	6.92	725	8.21	89.57	73.0	0.595
33.0	6.87	754	16.0	11042	142	0.941
55.0	7.03	787	32.9	14381	292	1.48

Table A5.2 : Adsorption experiment in which the background electrolyte was NaCl, at a concentration of 0.05 M.

$[\text{Cd}]_{\text{init.}}$ (mg/l)	$\text{pH}_{\text{equilib.}}$	$\text{EC}_{\text{equilib.}}$ (mS/cm)	C_{Cd} (mg/l)	q_{Cd} (mg/kg)	RSD (%)	$[\text{Cd}_f] \times 10^3$ (mmol/l)	$[\text{Cd}_f]/[\text{Cd}_b]$
0.11	6.95	5.78	<.05	71	-	-	-
1.09	6.86	5.77	0.343	485	2.3	3.10	0.459
2.18	6.83	5.76	0.782	906	1.2	6.96	0.559
3.27	6.77	5.91	1.35	1242	4.3	12.0	0.706
5.42	6.88	5.85	2.00	2221	0.4	17.8	0.586
7.59	6.70	5.88	4.16	2226	2.6	37.0	1.21
8.68	6.78	5.98	4.85	2486	0	43.1	1.27
9.75	6.76	5.79	5.72	2614	0.5	50.9	1.42
10.84	6.82	5.79	6.53	2794	7.1	58.1	1.51

Table A5.3 : Adsorption experiment in which the background electrolyte was NaCl, at a concentration of 0.5 M.

$[\text{Cd}]_{\text{init.}}$ (mg/l)	$\text{pH}_{\text{equilib.}}$	$\text{EC}_{\text{equilib.}}$ (mS/cm)	C_{Cd} (mg/l)	q_{Cd} (mg/kg)
0.11	7.18	43.0	0.069	670
2.20	7.20	43.0	1.35	555
3.30	7.18	43.2	2.10	781
4.40	7.24	43.0	2.84	1013
6.60	7.23	43.0	5.12	961
8.80	7.26	43.0	6.39	1559
11.0	7.11	43.1	7.53	2247
16.5	7.13	43.2	12.9	2351

Table A5.4 : Adsorption experiment in which the background electrolyte was Na₂SO₄, at a concentration of 0.025 M.

[Cd] _{init.} (mg/l)	pH _{equilib.}	EC _{equilib.} (mS/cm)	C _{Cd} (mg/l)	q _{Cd} (mg/kg)	[Cd _F] $\times 10^3$ (mmol/l)	[Cd _F]/[Cd _B]
0.11	7.12	4.59	0.02	58.5	0.178	0.222
2.20	7.18	4.60	0.311	1227	2.77	0.165
3.30	7.05	4.60	0.546	1789	4.86	0.198
4.40	6.97	4.62	0.823	2323	7.32	0.231
6.60	7.13	4.62	1.85	3083	16.5	0.391
8.80	7.02	4.66	2.89	3835	25.7	0.489
11.0	7.02	4.63	4.13	4458	36.7	0.601
16.5	7.10	4.64	8.63	5102	76.7	1.11

Table A5.5 : Adsorption experiment in which the background electrolyte was Na₂SO₄, at a concentration of 0.0167 M.

[Cd] _{init.} (mg/l)	pH _{equilib.}	EC _{equilib.} (mS/cm)	C _{Cd} (mg/l)	q _{Cd} (mg/kg)	[Cd _F] $\times 10^3$ (mmol/l)	[Cd _F]/[Cd _B]
0.11	7.06	3.20	< 0.05	68.2	-	-
2.20	7.00	3.16	0.273	1252	2.43	0.142
3.30	7.04	3.19	0.503	1817	4.48	0.180
4.40	6.97	3.20	0.782	2350	6.96	0.216
6.60	6.97	3.18	1.48	3330	13.2	0.289
8.80	6.99	3.16	2.33	4193	20.8	0.362
11.0	6.95	3.15	3.43	4913	30.5	0.453
16.5	6.90	3.15	6.73	6339	59.9	0.690

Table A5.6 : Adsorption experiment in which the background electrolyte was CaCl_2 , at a concentration of 0.025 M.

$[\text{Cd}]_{\text{init.}}$ (mg/l)	$\text{pH}_{\text{equilib.}}$	$\text{EC}_{\text{equilib.}}$ (mS/cm)	$C_{\text{Cd.}}$ (mg/l)	q_{Cd} (mg/kg)
0.11	6.97	4.87	0.091	12.3
2.20	7.11	4.90	1.80	259
3.30	6.98	4.99	2.65	422
4.40	6.95	4.96	3.85	357
8.80	7.03	4.92	8.37	276

Table A5.7 : Adsorption experiment in which the background electrolyte was CaCl_2 , at a concentration of 0.0167 M.

$[\text{Cd}]_{\text{init.}}$ (mg/l)	$\text{pH}_{\text{equilib.}}$	$\text{EC}_{\text{equilib.}}$ (mS/cm)	$C_{\text{Cd.}}$ (mg/l)	q_{Cd} (mg/kg)
0.11	7.04	3.32	0.077	21.4
2.20	6.96	3.33	1.58	404
3.30	6.83	3.33	2.43	568
4.40	6.90	3.31	3.34	692
6.60	6.84	3.33	5.16	939
8.80	6.80	3.34	7.18	1049
11.0	6.82	3.33	8.88	1371
16.5	6.87	3.33	13.9	1669

Table A5.8 : Data used for construction of Langmuir isotherms from adsorption experiments performed using a variety of background electrolytes at various concentrations. This data was obtained by simple manipulation of data in Tables 1-7.

NaCl 0.005 M		NaCl 0.05 M		NaCl 0.5 M		Na ₂ SO ₄ 0.025 M		Na ₂ SO ₄ 0.0167 M		CaCl ₂ 0.025 M		CaCl ₂ 0.0167 M	
1/c _{Cd}	1/q _{Cd}	1/c _{Cd}	1/q _{Cd}	1/c _{Cd}	1/q _{Cd}	1/c _{Cd}	1/q _{Cd}	1/c _{Cd}	1/q _{Cd}	1/c _{Cd}	1/q _{Cd}	1/c _{Cd}	1/q _{Cd}
3124720	163	328208	236	83176	202	361928	91.6	411384	89.8	62444	434	71229	278
1307212	82.1	143872	123	53952	144	205692	62.8	223676	61.8	42415	266	46331	198
446228	57.3	83176	91.0	39340	111	137128	48.3	143872	47.9	29195	315	36702	162
259644	43.6	56200	50.6	22480	117	60696	36.4	76432	33.7	13429	407	21804	120
144996	29.7	26976	50.6	17984	71.9	39340	29.3	48332	26.8			15666	107
87784	23.0	23154	45.2	14612	50.6	26976	25.2	32596	22.9			12658	82
60246	19.0	19670	43.0	8992	47.8	13488	22.0	16860	17.8			8081	67
35293	13.0	17197	40.2										

c_{Cd} = concentration of Cd at equilibrium (in mol/l)
q_{Cd} = amount of Cd adsorbed (in mol/kg)

Table A5.9 : Regression equations fitted to curves plotted in Figures 4.6 and 4.7.

Electrolyte	Regression equations from Table 4.6 ($y = [M_F]/[M_B]$, and $x = [M_F]$)		Regression equations from Langmuir plots, $y = 1/q$ and $x = 1/c$ (Figure 4.7)
	A*	B**	
0.005 M NaCl	$y = 0.057 + 0.0095x$	$y = 0.21 + 0.0045x$	$y = 10.9 + 0.00011x$
0.05 M NaCl	$y = 0.37 + 0.028x$	$y = 0.65 + 0.015x$	$y = 29.9 + 0.00063x$
0.5 M NaCl			$y = 37.6 + 0.0020x$
0.0167 M Na ₂ SO ₄	$y = 0.10 + 0.016x$	$y = 0.18 + 0.0085x$	$y = 18.3 + 0.00018x$
0.025 M Na ₂ SO ₄	$y = 0.12 + 0.017x$	$y = 0.17 + 0.012x$	$y = 21.4 + 0.00020x$
0.0167 M CaCl ₂			$y = 338 + 0.00048x$
0.025 M CaCl ₂			$y = 45.6 + 0.0033x$

* A = equation of regression curve fitted at low $[Cd_F]$ values

** B = equation of regression curve fitted at high $[Cd_F]$ values

Appendix 6

The percentage of Cd removed from solution by compost as a function of the initial Cd concentration

Table A6.1 : The percentage removal of cadmium from solution from initial concentration ($[Cd]_{initial}$) to equilibrium concentration (c_{Cd}), for the adsorption experiment in which the background electrolyte used was 0.0167 M Na_2SO_4 .

$[Cd]_{initial}$ (mg/l)	c_{Cd} (mg/l)	percentage removal
0.11	0.005	95.5
2.2	0.273	87.6
3.3	0.503	84.8
4.4	0.782	82.2
6.6	1.481	77.6
8.79	2.334	73.4
10.99	3.426	68.9
16.48	6.731	59.16

Appendix 7

Data for breakthrough curve reproducibility test

Table A7.1: Data for breakthrough curves for reproducibility tests. The pH variation with volume of 0.01 M NaOH solution passed through the column at a flow rate of 70 ml/hr.

Volume (ml)	pH		
	column 1	column 2	column 3
3.5	5.62	5.77	5.66
11.6	6.34	6.33	6.24
38.1	6.80	7.02	7.03
72.9	7.71	7.84	7.93
96.0	8.97	8.87	9.08
119	10.19	9.94	10.10
177	11.65	11.16	11.21
235	11.83	11.52	11.56
293	11.92	11.80	11.67
350	11.99	11.87	11.68

Appendix 8

Experimental data for the construction of breakthrough curves

Adsorption

Table A8.1 : Column effluent cadmium concentrations as a function of the volume of 5.54 mg/l cadmium solution passed through the column at a flow rate of 80 ml/hr.

volumes (ml)	[Cd] (mg/l)	volumes (ml)	[Cd] (mg/l)
409	0.022	3386	1.819
818	0.007	3551	1.979
1227	0.004	3715	2.116
1636	0.010	3879	2.176
1841	0.027	4044	2.44
1939	0.113	4208	2.695
2038	0.136	4373	2.935
2136	0.266	4537	2.795
2235	0.368	4701	3.025
2333	0.528	4866	3.61
2432	0.623	5030	3.28
2531	0.829	5195	3.43
2630	0.970	5523	3.56
2729	1.225	5688	3.75
2893	1.177		
3057	1.379		
3222	1.637		

Desorption

Table A8.2 : The desorption of Cd from the compost column as a function of volume of 0.05 M NaCl passed through the column. Note that the volume data, are added on to those from the breakthrough curve, and thus are not the true volumes of NaCl passed through the column.

volumes (ml)	[Cd] (mg/l)
6345	3.81
6674	3.81
6915	3.76
7042	3.48
7282	2.96
7881	2.34
9481	1.65
11081	1.18
12841	1.06
13961	0.91